

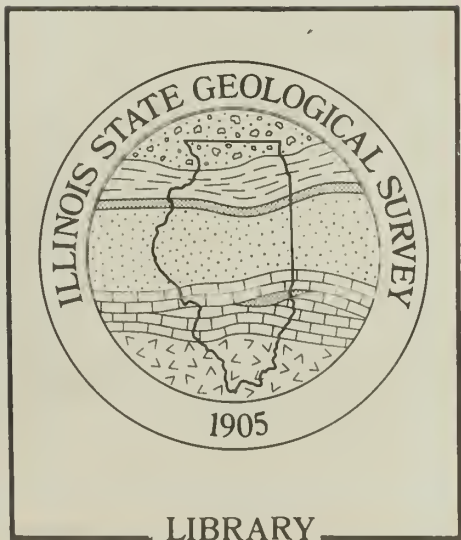
Groundwater Contamination in Karst Terrain of Southwestern Illinois

S.V. Panno, I.G. Krapac, C.P. Weibel, and J.D. Bade

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Cover photo Ponded sinkholes surrounding a farm in Monroe County.

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EXECUTIVE SUMMARY

The pervasiveness of groundwater contamination in southwestern Illinois has been attributed by local health officials to the presence of karst terrain. Karst features such as sinkholes act as direct pathways for surface waters, septic discharge, and other contaminants to the shallow karst aquifer, thereby avoiding the cleansing mechanisms provided by the soil and substrates.

Groundwater samples were collected from nine springs, one cave stream, and 33 bedrock wells from January 1994 to February 1996 to evaluate the degree and geographic extent of groundwater contamination in the karst terrain of rural southwestern Illinois. The samples were analyzed for temperature, pH, Eh (reduction-oxidation potential), specific conductance, alkalinity, cations and anions, bacteria (total coliform, fecal coliform, enterococcus, total aerobic bacteria, and bacterial species), and the pesticides alachlor and atrazine. Also examined were water quality data on private wells collected by the Monroe-Randolph Bi-County Health Department (MRCHD) from 1986 to 1995.

Most springs contained large concentrations of coliform, fecal coliform, enterococcus, and a variety of other bacterial species as well as anomalously large concentrations of nitrate (NO_3^-) and trace levels of pesticides throughout the year. Bacterial species present indicate that bacteria originate from both human and livestock sources. These bacteria could pose a health risk to people coming in contact with the spring water. Nitrate concentrations in water samples from springs rarely exceeded the U.S. Environmental Protection Agency (U.S. EPA) regulatory limit of 10 mg/L (as N). Alachlor and atrazine concentrations in these samples often exceeded the U.S. EPA Maximum Contaminant Levels of 2.0 and 3.0 $\mu\text{g/L}$, respectively, during and following spring rainfalls.

Twenty-nine of the 33 wells sampled were selected at evenly spaced locations along three east-west transects across Monroe and Randolph Counties and sampled in April, July, October (all 1995), and February (1996). Coliform bacteria were found in 62% of the July samples, but only in 28% of the April samples and 21% of the October and February samples. These data suggest that warmer summer temperatures fostered bacterial growth in the regolith (all material overlying bedrock) as well as in the shallow aquifers and in the surface and near-surface water recharging the shallow karst aquifer. The NO_3^- concentrations in the well samples remained nearly constant throughout the year; only two transect wells (7%) contained NO_3^- concentrations that exceeded 10 mg/L. Pesticides were detected in groundwater samples from wells most frequently in April, when pesticides were being applied to croplands.

Long-term water quality data from the MRCHD files indicate that there was a sharp increase in the proportion of wells in Monroe County containing coliform bacteria in about 1987. This increase in bacterial contamination coincided with an increase in residential development in the county. Bacterial species found in wells and springs indicate that private septic systems are a significant source of bacterial contamination of the shallow karst aquifers in the study area.

A comparison of water samples from springs and wells suggested that the chemical and bacterial composition of water from some wells was similar to the water from most springs. Because of (1) the similarities of groundwater in both shallow and deep wells and (2) the fact that the presence and concentrations of surface-borne contaminants in samples from springs and wells appeared to be seasonally dependent, movement of groundwater from shallow karst aquifers into the deeper wells is likely. Well construction techniques allow all sources of groundwater (both shallow and deep) to enter some wells, thus allowing contaminants from the shallow karst aquifer also to enter the wells. Well construction techniques that may help alleviate some of the water quality problems are recommended, as is the redirection of effluent flow from septic systems that discharge into sinkholes.

INTRODUCTION

Problem

Groundwater contamination in southwestern Illinois is a serious problem because the karst terrain that dominates some areas in this part of the state readily allows contaminants to reach groundwater. Sinkholes, springs, caves, and disrupted surface drainage are the most obvious features in a karst landscape (White 1988). These features result from the presence of water-soluble carbonate bedrock (e.g., limestone and dolomite) and relatively thin soil cover. Fractures in the carbonate bedrock are enlarged as soil waters, enriched in carbon dioxide that forms carbonic acid, slowly dissolve the rock as the water migrates into and through the rock. The fracture boundaries dissolve to a point where the overlying soil can no longer bridge their gap and the soil collapses into the



Figure 1 Freshly formed cover-collapse sinkhole (diameter = 5.7 m [19 ft], depth = 5.0 m [16 ft]) having white limestone epikarst, reddish limestone, and gray limestone near the base. The hole at the base of the sinkhole is a conduit entering a cave system. Erosion will eventually reduce the fresh sinkhole to a bowl-shaped depression with a central drain.

enlarged fracture (fig. 1). Shallow aquifers in karst terrain contain relatively large pores that, because they are connected to the surface via sinkholes, often preclude the natural cleansing processes that normally occur when surface-derived water slowly infiltrates into the groundwater system through soil. Recharge of shallow karst aquifers may occur in seconds or minutes, and surface-derived contaminants (e.g., waste from septic systems, agricultural chemicals, and livestock waste) may enter the aquifer.

The densest concentrations of karst features in the state are found in Monroe, Randolph, and St. Clair Counties (fig. 2) (Weibel and Panno, in press). Concentrations of total coliform bacteria, fecal coliform bacteria, and nitrate (NO_3^-) in water samples collected from wells in Monroe and Randolph Counties frequently exceed U.S. Environmental Protection Agency (U.S. EPA) quality standards for drinking water. Trace concentrations of pesticides have also been detected in water samples collected from residential wells and springs (Panno et al. 1995).

The Monroe-Randolph Bi-County Health Department (MRCHD) has estimated that about 50% of the residents of Monroe and Randolph Counties depend on groundwater as their primary source of drinking water. The MRCHD has also estimated that approximately two-thirds of the wells in these counties are contaminated with coliform bacteria and that approximately 10% are contaminated with unacceptably large concentrations of NO_3^- . This problem has forced many residents who rely on well water to use bottled water for drinking.

The demand for good quality water is increasing in the study area. Recent highway improvements in Monroe County have reduced commuting times between the northern part of the county and St. Louis, thus making the area a more desirable place to live. Land use is beginning to shift from rural agricultural to residential, resulting in increased groundwater use and protection problems and raising questions regarding proper disposal of septic waste. A better understanding of the degree, extent, and underlying causes of the water quality problems is vital because of the potential for further growth and increased water use in the study area.



Figure 2 Aerial view of a typical area within the sinkhole plain in Monroe County. Sinkholes are marked by slight depressions, ponds, and tree clusters.

Purpose

An evaluation of groundwater contaminants in southwestern Illinois was undertaken because of known human health problems associated with coliform bacteria (e.g., Craun 1979, Pontius 1992), NO_3^- (O’Riordan and Bentham 1993), and pesticides (Kelce et al. 1995, Biradar and Rayburn 1995). The purpose of this study was to investigate the nature, magnitude, and spatial variability of groundwater contamination in Monroe and Randolph Counties. The investigation included sampling groundwater from springs, cave streams, and bedrock wells. Because little work had been conducted in the study area prior to this investigation, none of the groundwater basins had previously been defined and the verified locations of resurgent springs from only a few large caves had been identified (e.g., Frasz 1983). Thus, the determination of the sources of contaminants in springs was usually limited to only a few known flow patterns. The results of this investigation could be used to design more effective groundwater sampling strategies for the local health department and other concerned organizations. The results could also lead to steps toward mitigating groundwater contamination problems in these counties.

BACKGROUND

Groundwater Contamination

Groundwater in karst regions is very susceptible to contamination because the fractured and honeycombed nature of karstified carbonate rock commonly provides a direct connection between surface water and groundwater. Recharge to the water table in these regions is often nearly instantaneous, and the infiltrating water does not have the benefit of the slow filtration through fine-grained materials that allows for chemical, biological, and physical degradation and attenuation of potential contaminants (White 1988, Ford and Williams 1992). This lack of filtration and the nearly ubiquitous presence of agrichemicals and septic systems in the study area have probably resulted in the presence of coliform and fecal coliform bacteria, NO_3^- , and pesticides in water samples from springs and wells.

Coliform and fecal coliform bacteria commonly are used as indicators of the potential presence of other pathogens (Clesceri et al. 1989). McFeters and Stuart (1972) stated that "the occurrence of fecal coliform bacteria in water is regarded as the single most important indicator of public health hazard from infectious agents." An increase in autoimmune diseases in this country and an increase in the percentage of elderly in the population have resulted in an increase in the number of people with less tolerance for bacterial and viral agents (E.C. Stormont, Illinois Department of Agriculture Animal Disease Laboratory, personal communication, 1996). Thus, the prevalence of waterborne pathogens in the drinking water supply of rural areas may become an increasingly serious problem (Cason et al. 1991).

Nitrate contamination in groundwater is a national issue because it may be a byproduct of fertilization of croplands with solid fertilizer, manure, liquid anhydrous ammonia, or urea. Nitrogen in soil is necessary for plant growth. Its availability to plants is limited by organic reactions that are often too slow and inefficient to meet production demands. Other sources of NO_3^- include effluent from private septic systems and livestock wastes. Nitrate in drinking water can cause *methemoglobinemia* (blue-baby syndrome) and possibly stomach cancer (O'Riordan and Bentham 1993).

Herbicides and insecticides are applied extensively to croplands in Illinois. Herbicides are applied to an estimated 97% of the corn and 96% of the soybean acreage of Illinois (U.S. Department of Agriculture 1991). Because pesticides are subject to leaching and runoff, they are capable of degrading water quality, especially in karst terrain where runoff may enter groundwater in a matter of seconds to minutes.

Geologic and Hydrogeologic Settings

Monroe and Randolph Counties may be divided into two areas on the basis of topography: the Mississippi River valley (to the west) and the upland area (to the east). The boundary between these areas is marked by bluffs of Mississippian-age limestone that commonly exceed 60 m (200 ft) in height. The upland region adjacent to the Mississippi River just south of East St. Louis, including southern St. Clair, most of Monroe, and northern Randolph Counties, is often referred to as the "sinkhole plain" because of its large density of sinkholes (fig. 3a). The upland area of Monroe and Randolph Counties was the focus of this investigation.

Bedrock in these counties consists predominantly of Mississippian limestone and dolomite, in addition to lesser amounts of Mississippian and Pennsylvanian limestone, sandstone, shale, claystone, and coal (fig. 3b). In the western part of these counties, loess and residuum are mostly absent, and bedrock is exposed at and near the Mississippi River bluffs (Herzog et al. 1994). Where loess and residuum occur, they are typically less than 15 m (50 ft) thick, but they may be thicker in and near stream valleys (Piskin and Bergstrom 1975).

Monroe and Randolph Counties are on the western margin of the Illinois Basin, and the bedrock generally dips gently to the east toward the center of the basin. Two parallel structures, the Waterloo-Dupo Anticline and the Columbia Syncline, trend northwest-southeast (fig. 3a) within Monroe County and intersect the southwestern part of St. Clair County (Treworgy 1981). The Valmeyer Anticline, subparallel to these structures, is entirely within Monroe County (fig. 3a). The distribution of karst terrain in Monroe County (Panno et al. 1995) is influenced by these structural features (Panno et al., in press). The geomorphology of the land surface along the axis of the Columbia Syncline is controlled by a layer of Pennsylvanian bedrock overlying karstic Mississippian limestone (fig. 3b). The Pennsylvanian bedrock is predominantly shale and effectively separates underlying karst limestone from the above regolith (including soil, glacial drift, and residuum), which would otherwise be susceptible to collapse into void spaces in the limestone. The terrain on the northeastern flank of the Valmeyer Anticline contains no karst features at the land surface (Panno et al. 1995), even though the bedrock along this anticline is Mississippian limestone (fig. 3a).

Sinkholes in the study area occur in the regolith overlying the Mississippian limestone bedrock, whereas caves occur within the bedrock. The bedrock ranges from the Salem Limestone to the limestones of the Pope Group (fig. 3b). No karst features were observed where Pennsylvanian shale overlies the Mississippian strata. Most of the sinkholes (Weller 1939) and caves occur in association with the St. Louis (fig. 4) and Ste. Genevieve Limestones.

Caves typically have formed by dissolution of limestone along its bedding planes and are common throughout the karst terrain of the study area (e.g., Illinois Caverns, Krueger's Dry Run Cave; fig. 5). Sinkholes are abundant in the regolith overlying karst features in the St. Louis and Ste. Genevieve

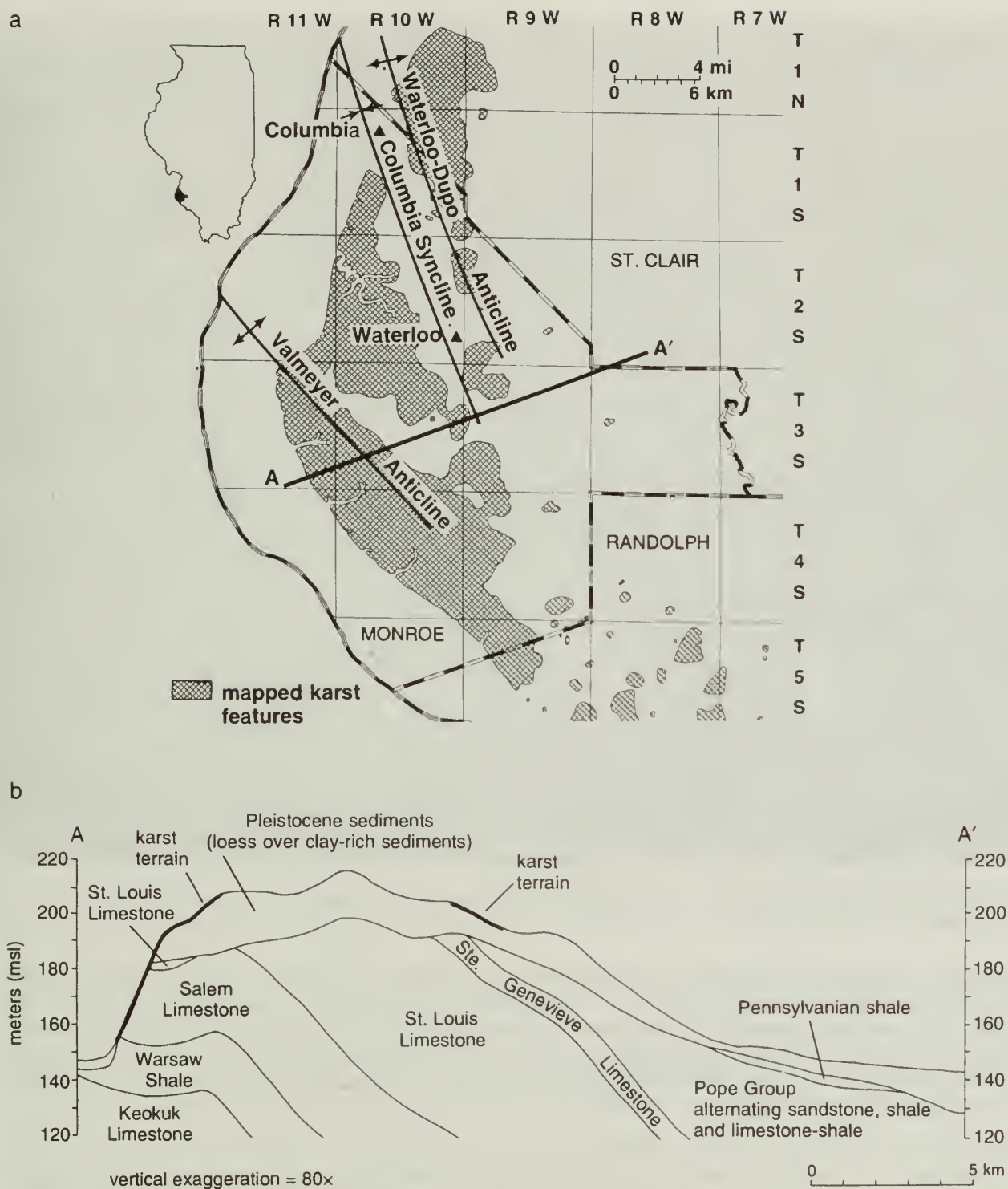


Figure 3 Karst terrain and associated structural features in the study area as shown in (a) map view, which shows the distribution of karst features and major structural features, and (b) cross section (A–A'), which shows the stratigraphy and major rock units. Locations of structural features are from Treworgy (1981).

Limestones and in the Salem Limestone. Sinkholes also occur, although less frequently, to the east in regolith overlying karst features in the Pope Group within the basal Paint Creek Formation, in the Beech Creek Limestone and Fraileys Shale Members of the Golconda Formation, and in the Vienna Limestone. A few sinkholes were found in regolith overlying the Cypress Sandstone, but these probably formed by dissolution and collapse of limestone in the underlying Paint Creek Formation (Panno et al. 1994b).

The upland area of Monroe and Randolph Counties is, for the most part, covered by a layer of loess that overlies both diamicton and bedrock residuum. Approximately one-third of the upland part of Monroe County has been mapped as karst terrain (Weibel and Panno, in press). Sinkholes



Figure 4 Exposure of the St. Louis Limestone in Monroe County showing solution features along bedding planes and cross-cutting bedding from the surface.

commonly formed where clay-rich regolith overlying karst carbonate rock was less than 7.5 m (25 ft) thick, regardless of the thickness of overlying silt and loess (Panno et al. 1994b), and where the water table had been lowered to below the soil-bedrock interface. Karst terrain typically appears near features that are responsible for lowering the water table, such as bluffs, stream valleys, and large cave systems. We suggest that this lowering of the water table initiated the formation of regolith-collapse sinkholes in southwestern Illinois.

Groundwater resources in these counties are found in Mississippian strata that include the St. Louis Limestone in the western part of the study area and the Aux Vases Sandstone and overlying limestones and sandstones of the basal Pope Group in the eastern part of the study area (fig. 3b). The St. Louis Limestone is not only the primary host for the karst topography, but some springs and many wells in this limestone are sources of groundwater for residents and small municipalities. The Aux Vases Sandstone is also a reliable source of groundwater to the east where it underlies part of the karst terrain and lies below thin glacial drift.

Land Use and Agricultural Practices

The climate in Monroe and Randolph Counties is temperate with a mean annual precipitation of approximately 102 cm (40 in.) (Wendland et al. 1992). The counties are predominantly rural, and land use is dominantly agricultural (fig. 6). A study published in 1977 found that 86% of Monroe County was farmland (SWIMPAC 1977), 70% of which was cropland (U.S. Department of Agriculture 1987). Only 44% of Randolph County, however, was used as farmland (SWIMPAC 1977). Crops grown in the region include milo, alfalfa, soybeans, wheat, corn, and barley. Insecticides used on alfalfa include carbaryl, carbofuran, chlorpyrifos, malathion, permethrin, and phosmet. They are typically applied in May and again in July or August. Herbicides are applied in April and May only.



Figure 5 One of three large caves found in Monroe County. The stream occupying this sinuous passage drains the groundwater basin surrounding the cave system (photo by Brian T. Schaffner).

They include alachlor, atrazine, bentazon, chlorimuron, cyanazine, glyphosate, imazaquin, imazethapyr, metolachlor, sethoxydim, and trifluralin (M. Roegge, Cooperative Extension Service, University of Illinois, personal communication, 1993). Additional chemicals applied to the soils include fertilizers such as anhydrous ammonia, potash, and phosphate. These fertilizers are applied once or twice per year, usually in the spring and fall, depending on the crop rotation schedule and in conjunction with pesticide applications in the spring (W. Sensel, farmer, personal communication, 1994).

EXPERIMENTAL METHODS

A total of 325 groundwater samples was collected from nine springs, one cave stream (Illinois Caverns), and 33 wells (fig. 7) from January 1994 to February 1996. Because most springs discharge from caves, cave streams will be referred to as springs for simplicity. The sites were selected on the basis of geographic distribution and our ability to obtain the permission of land-owners to sample their wells and springs. A detailed discussion of site selection as well as a description of each well and spring site is given in the appendix. Several of the springs and wells were repeatedly sampled during and following rainfall events in 1994 because spring rains wash pesticides from the fields and maximum concentrations can be found at this time. Samples from springs (four of which were not sampled until 1995) were collected on a monthly basis. Three of the 33 wells were selected because they were known to contain coliform bacteria and large concentrations of NO_3^- . Twenty-nine of the wells were selected, without prior knowledge of water quality, at approximately equally spaced locations along three east-west transects across the two counties (in karst and nonkarst terrain). These wells were sampled three times at 3-month intervals during 1995.

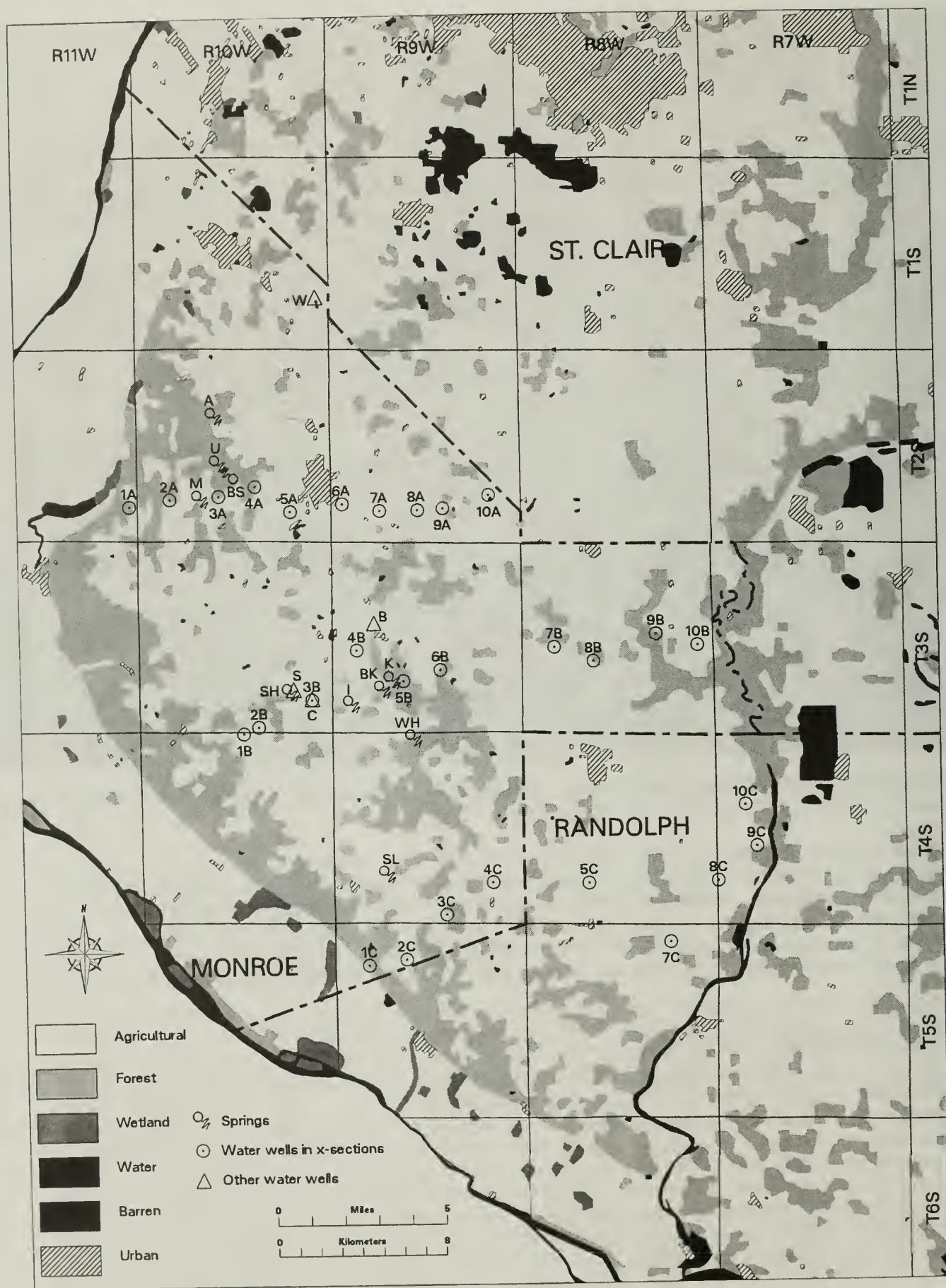


Figure 6 Map of the land use and sampling locations in the study area.

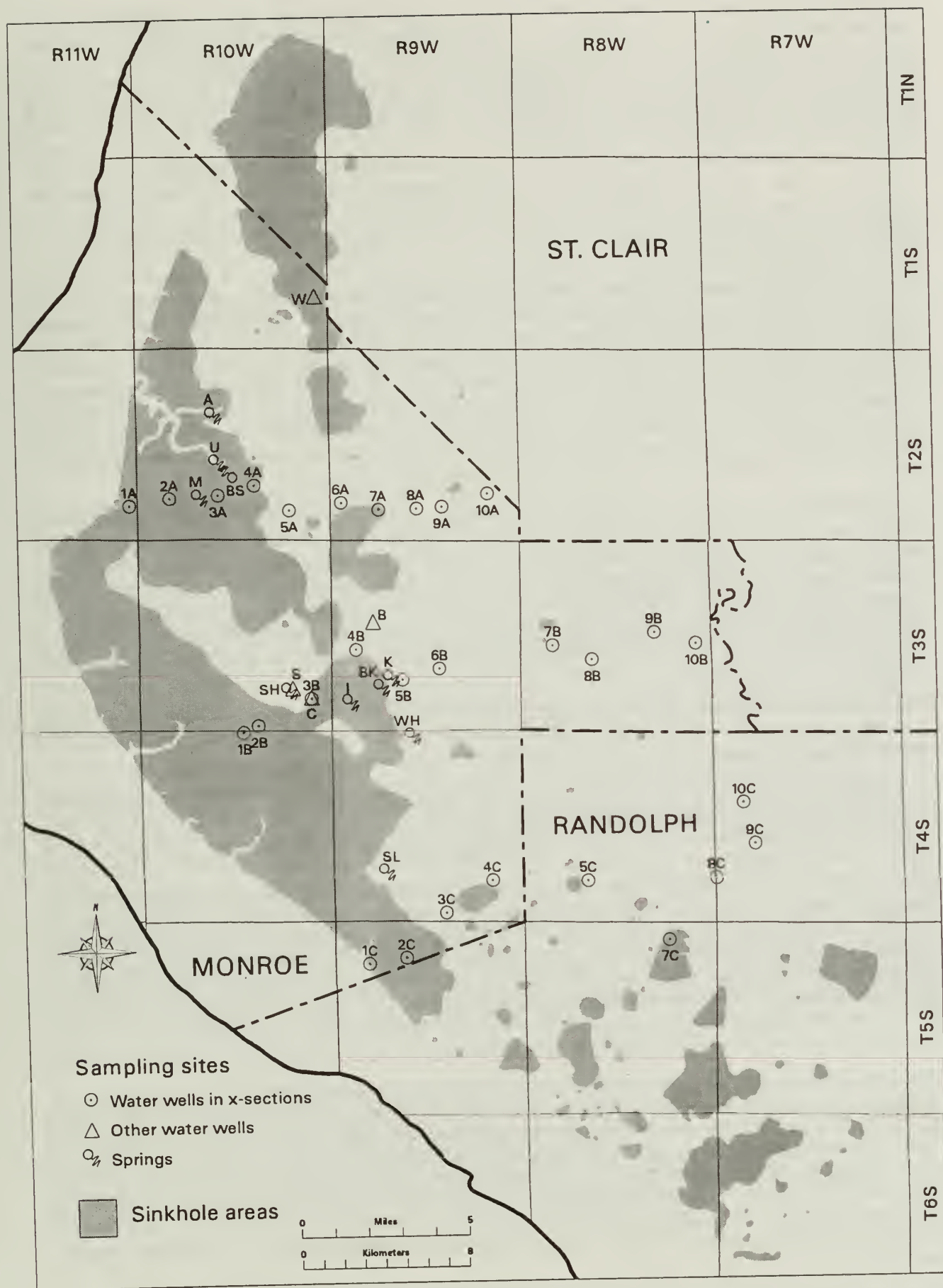


Figure 7 Map of the study area showing karst regions (sinkhole areas) and sampling locations. Locations and identifiers of springs and wells are given in tables 1 and 2.

All water samples were analyzed in the field for temperature, pH, and specific conductance. All samples were analyzed in the field for Eh in 1994, but only well water samples were all analyzed for Eh in 1995 and 1996. The 1994 testing showed that the spring water had equilibrated with the air by the time it reached the spring, and Eh measurements were unnecessary. Field measurements for pH and specific conductance were made using meters that allowed temperature compensation, and all instruments were calibrated with appropriate standards at each sampling site.

Groundwater samples were collected in accordance with field techniques described in Wood (1981) and represented both time-integrated and grab samples. Water samples from wells at private residences were collected from outdoor faucets that bypassed water-treatment units. Water was allowed to run until pH, Eh, temperature, and specific conductance readings stabilized, and then water samples were collected.

All water samples were analyzed in the laboratory for cations, anions, and bacteria. Samples collected for cations, anions, and alkalinity were filtered through 0.45- μ m membranes and stored in polyethylene bottles. Samples analyzed for cations were acidified in the field with ultra-pure nitric acid to a pH of 2.0. Samples collected for pesticides were unfiltered and stored in 60-mL, precleaned, amber glass bottles. The samples were transported in ice-filled coolers to the laboratory and kept refrigerated at approximately 4°C until analyses had been completed. Samples collected for pesticide analysis were filtered in the laboratory prior to analysis. Alkalinity was determined on spring water samples in 1994 only and on the well transect samples in both years. Samples analyzed for pesticides and alkalinity were processed within 2 to 3 days of collection.

Samples collected for bacterial analysis were stored in sterilized 250-mL bottles and analyzed within 24 hours for total coliform, fecal coliform, total (other) bacteria, and bacterial species using standard techniques (Clesceri et al. 1989). Initially, bacterial concentrations greater than 200 colonies/100 mL of water were reported as too numerous to count (TNTC). Samples collected in 1995 were diluted in order to obtain better counts of bacterial concentrations. The presence of coliform and fecal coliform bacteria may have been masked in water samples containing greater than 80 colonies of "other bacteria"/100 mL of water (S. Peters, TEKLAB, INC., Collinsville, IL, personal communication, 1995).

Determination of bacterial species was conducted at the Illinois Department of Agriculture Animal Disease Laboratory (Centralia, IL) using standard methods to isolate and identify bacterial colonies present (Clesceri et al. 1989, Cason et al. 1991).

Groundwater samples were collected at the mouths of springs using an ISCO™ 3700 automatic sampler, seepage samplers (Panno et al. 1994a, Panno et al., unpublished data), and grab samples. Water samples collected with the ISCO™ sampler were composite samples in which 150-mL samples were collected every 30 minutes over a 12-hour period and combined in one sample bottle. Four samples were collected in four liter-size glass sample bottles using this sampling protocol. Composite water samples collected with seepage samplers were collected for 2- to 24-hour periods in 1994 and for 1-month periods in 1995. Water quality data from each spring were treated as a single data set for descriptive purposes even though they may represent water samples collected for different time periods and under different climatic conditions. This practice was an effective means of identifying the degree and extent of contamination for the purposes of this investigation. Grab samples represent instantaneous samples of spring water, and they were collected monthly from each spring to bracket the long-term samples.

Because Alachlor and atrazine are the most commonly used herbicides in the study area (M. Roegge, Cooperative Extension Service, University of Illinois, personal communication, 1993), these herbicides were deemed to be representative of pesticide contamination in southwestern Illinois. Atrazine is also the most persistent pesticide in the Midcontinental United States (Goolsby 1991). Water samples were analyzed for atrazine and alachlor using enzyme-linked immunosorbent assays (ELISA). The ELISA technique has been found to yield data that correlate well with samples analyzed using gas chromatography/mass spectrometry techniques (Thurman et al. 1990). Blanks, spikes, and replicate samples were collected each time water samples were collected from the selected sites.

Concentrations of cations were analyzed using a Model 1100 Thermo-Jarrell Ash Inductively Coupled Argon Plasma Spectrometer (ICAP). Instrument control, automatic background correction, and spectral interference corrections were performed using a DEC Micro PDP 11/23 computer.

Solution concentrations of anions were determined using a Dionex 211i ion chromatograph, following U.S. EPA Method 300 (O'Dell et al. 1984).

Archived data on coliform bacteria and NO_3^- concentrations in well water samples from the files of the MRCHD were reviewed and plotted on karst maps of Monroe County. These well samples were collected by health department personnel and homeowners. Homeowners were given precleaned sample bottles and instructions on how to obtain the sample. Two laboratories determined total coliform bacteria and NO_3^- concentrations in these samples; detection limits for NO_3^- as N for the two laboratories were ≤ 5 mg/L and ≤ 10 mg/L.

Land-use data (LUDA) were used to construct a land-use map for this investigation. Land-use data were derived from the U.S. Geological Survey (USGS) nationwide mapping of land use and land cover (Anderson et al. 1976). The data were interpreted from National High Altitude Program photographs, as well as from other high-altitude photographs, and were digitized onto 1:250,000-scale (1 inch = 4 miles) maps. The remote sensing data were collected from 1972 to 1981. Most of the data presented are from the 1:250,000-scale St. Louis Quadrangle, for which data were collected in 1972 and 1976. Data from the Belleville Quadrangle (collected 1980), the Rolla Quadrangle (collected 1978), and the Paducah Quadrangle (collected 1973) were also included. The land-use categories given are USGS Level 1 categories, which were the most generalized in the LUDA program. The minimum resolution for the LUDA program was 40 acres in rural areas and 10 acres in urban areas.

RESULTS AND DISCUSSION

Groundwater Chemistry

Summary statistics of field parameters, major cations and anions, and bacterial and pesticide concentrations of all springs and of wells W, C, B, and S are presented in table 1. These statistics represent water samples collected from January 1994 to February 1996. The chemical composition of groundwater in the study area is typical of most groundwater in contact with limestone. Groundwater samples from springs in the study area were predominantly Ca^{2+} - HCO_3^- -type water (fig. 8). Groundwater samples from deeper wells and wells in the eastern and southeastern parts of Monroe and the eastern part of Randolph Counties (appendix: fig. A2) were more typically Na^+ - HCO_3^- -type water (fig. 8).

The pH of all samples ranged from 6.1 to 8.5, and Eh measurements indicated that groundwater in the karst aquifer was open to the atmosphere for all springs and all but a few wells. Field parameters, specifically temperature and specific conductance, were used to determine the hydraulic connections of adjacent springs and karst windows (Shuster and White 1971) as well as to indicate, qualitatively, surface runoff and base-flow conditions.

The largest variability observed in the chemical composition of spring water occurred during and following rain events that initiated runoff. It is well known that surface runoff entering the flow systems of karst springs moves through the systems rapidly. Simple dilution and entrainment of surface contaminants dominate the water quality of spring discharge during rain events (White 1988). Typically, specific conductance is smallest during peak flow of a spring as a result of dilution of ionic constituents. The water samples containing the largest concentrations of agrichemicals were collected immediately following peak flow periods. The maximum and minimum concentrations of constituents in spring samples (table 1) were the result of rainfall and runoff.

Alkalinity and specific conductance typically vary together in groundwater in carbonate terrains and reflect the ionic strength of groundwater in carbonate aquifers (White 1988, Jacobson and Langmuir 1970). Thus, alkalinity values for groundwater from carbonate aquifers in southwestern Illinois can be calculated from specific conductance measurements. Regression analysis of 110 field measurements of specific conductance and alkalinity made in 1994 indicates that alkalinity can be estimated from measured conductivity values using the following equation:

$$Y = 0.42X - 15, (r^2 = 0.91)$$

where

Y = alkalinity as mg/L CaCO_3 and

X = specific conductance in $\mu\text{S}/\text{cm}$

Table 1 Descriptive statistics of groundwater chemistry data from selected wells and all springs sampled (alkalinity and all ionic constituents reported in mg/L).

Location (Sec., T., R.)	Name	Temp. (°C)	pH	Eh (mV)	Sp.cond. (µS/cm)	Tot. alk. as CaCO ₃	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SiO ₂	NO ₃ ⁻ -N	SO ₄ ²⁻	Cl ⁻	Colonies (other) per 100 mL	Colif. per 100mL	Fecal colif. per 100mL	Alachlor (µg/L)	Atrazine (µg/L)
25,1S,10W	Well W	Max.	16.2	6.9	460	868	351	2	127	33	33	4.67	45	83	3000	2000	0	BDL	0.11
		Min.	14.8	6.4	261	622	200	BDL	93	13	15	2	36	41	146	28	0	BDL	BDL
		N	10	10	8	10	10	10	10	10	9	9	10	10	7	7	1	10	10
		Avg.	15.24	6.689	363.1	735.8	268.0	1.26	113.6	17.5	29.3	3.35	40.0	52.2	ND	ND	ND	BDL	0.016
		Std.	0.49	0.149	56.94	72.70	46.18	0.651	11.58	5.394	5.14	0.824	2.307	11.86	ND	ND	ND	ND	0.032
26,3S,10W	Well C	Max.	14.1	7.2	463	824	326	2	104	57	20	14.2	38	25	TNTC	52	0	0.23	0.46
		Min.	12.7	6.8	243	783	321	BDL	91	21	9	3.7	36	22	0	0	0	0.14	BDL
		N	10	9	8	10	10	10	10	10	9	10	10	10	7	7	1	10	10
		Avg.	13.60	6.984	386.5	799.1	323.7	0.79	96.0	26.9	18.1	10.8	36.9	23.2	ND	ND	ND	0.181	0.071
		Std.	0.368	0.107	61.72	10.98	1.656	0.661	3.356	9.911	3.358	2.658	0.638	0.768	ND	ND	ND	0.032	0.136
17,3S,9W	Well B	Max.	15.7	7.1	424	1140	465	1	124	40	26	12.5	137	48	40	40	0	BDL	BDL
		Min.	14.1	6.8	200	1093	390	BDL	109	37	12	8.6	104	43	0	0	0	BDL	BDL
		N	7	7	6	7	7	7	7	7	6	7	7	7	6	6	1	7	7
		Avg.	14.67	6.954	368.3	1115	416.0	0.61	115.0	38.4	22.3	10.4	115.4	44.9	ND	ND	ND	BDL	BDL
		Std.	0.52	0.068	79.87	13.38	28.54	0.338	4.78	1.108	4.848	1.298	10.49	1.914	ND	ND	ND	ND	ND
26,3S,10W	Well S	Max.	14.8	7.2	233	836	432	BDL	102	41	18	0.15	29	14	3100	0	ND	BDL	BDL
		Min.	14.0	6.1	-46	795	420	BDL	96	39	8	0.003	26	12	20	0	ND	BDL	BDL
		N	4	4	4	5	5	5	5	5	4	5	5	5	4	4	0	5	5
		Avg.	15.58	6.817	142.9	819.5	426.4	ND	99.8	39.8	15.3	0.09	27.0	12.7	ND	ND	ND	BDL	BDL
		Std.	2.177	0.419	113.6	15.61	3.826	ND	1.925	0.868	4.193	0.049	1.142	0.637	ND	ND	ND	ND	ND
26,3S,10W	Solich Spring	Max.	13.4	7.7	470	794	330	1	92	27	20	10.9	39	24	2400	0	ND	0.16	0.13
		Min.	13.1	6.8	240	768	320	BDL	83	25	8.8	1.3	37	20	0	0	ND	BDL	BDL
		N	9	9	8	9	9	9	9	9	8	9	9	9	8	8	0	9	9
		Avg.	13.26	7.182	384.1	782.5	323.9	0.543	85.9	26.0	18.0	7.95	37.7	21.7	ND	ND	ND	0.099	0.019
		Std.	0.094	0.225	61.46	7.636	3.348	BDL	2.488	0.747	3.462	3.040	0.707	0.998	ND	ND	ND	0.053	0.039
21,2S,10W	Boy Scout Camp Spring	Max.	16.4	8.2	456	645	285	5	100	21	23	3.8	41	15	TNTC	TNTC	ND	7.5	15.2
		Min.	11.9	6.5	260	95	36	BDL	12	2.6	6.4	0.6	6.2	2.7	TNTC	330	ND	0.13	BDL
		N	10	10	8	10	10	10	10	10	9	10	10	10	6.0	9	0	10	10
		Avg.	13.73	7.511	387.1	382.2	156.3	2.93	56.9	11.4	13.8	2.23	24.4	8.60	ND	ND	ND	1.131	3.045
		Std.	1.254	0.408	55.81	176.3	81.98	1.384	27.27	5.908	4.694	1.055	11.42	3.832	ND	ND	ND	2.136	5.184
21,2S,10W	Unnamed Spring	Max.	20.0	8.1	457	587	230	5	84	15	34	3.32	42	42	TNTC	TNTC	ND	3.28	20.4
		Min.	12.4	6.9	187	102	36	2	14	2.6	9.5	1.95	6.5	2.4	TNTC	TNTC	ND	0.43	0.88
		N	10	10	9	10	10	10	10	10	9	9	10	10	3	3	0	10	10
		Avg.	15.60	7.544	362.2	396.8	148.7	3.69	55.6	10.8	15.0	2.58	27.6	14.5	ND	ND	ND	1.270	5.795
		Std.	2.793	0.312	76.34	177.4	68.32	0.991	24.68	5.018	6.307	0.492	12.91	11.44	ND	ND	ND	1.081	6.668

Table 1 Continued

Location Sec., T., R.	Name		Temp. (°C)	pH	Eh (mV)	Sp.cond. (µS/cm)	Tot. alk. as CaCO ₃	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SiO ₂	NO ₃ ⁻ -N	SO ₄ ²⁻	Cl ⁻	Colonies (other) per 100 mL	Colif. per 100mL	Fecal colif. per 100mL	Alachlor (µg/L)	Atrazine (µg/L)	
16,2S,10W	Andy's Run Spring	Max.	20.8	8.0	360	730	293	37	5	99	18	24	5.47	41	23	3000	1000	24	0.1	0.2	
		Min.	13.2	7.0	351	140	45	3.3	BDL	16	3.4	6.8	1.02	6.6	5.0	0	200	2	BDL	BDL	
		N	10	10	2	10	10	10	10	10	10	10	10	10	10	10	1	2	2	10	10
		Avg.	14.62	7.473	355.5	601.9	238.9	28.6	1.60	82.6	15.0	20.1	3.99	35.1	19.5	ND	ND	ND	0.013	0.131	
		Std.	2.844	0.334	ND	160.0	67.20	9.611	1.657	22.13	4.00	4.664	1.528	9.28	5.523	ND	ND	ND	0.026	0.063	
29,2S,10W	May Spring	Max.	19.4	7.9	348	643	256	25	8	97	15	27	7.53	35	38	7000	4000	110	8.1	6.7	
		Min.	11.4	7.2	ND	165	55	3.5	BDL	21	3.8	10	2.16	9.1	6.0	0	2000	68	BDL	0.15	
		N	12	12	1	12	12	12	12	12	12	12	12	12	12	12	1	2	2	12	12
		Avg.	14.85	7.605	ND	509.3	199.9	19.0	2.91	76.0	11.4	21.1	5.70	26.7	16.2	ND	ND	ND	1.445	1.937	
		Std.	2.255	0.227	ND	136.0	57.15	6.219	2.131	21.09	2.914	4.561	1.738	6.873	7.521	ND	ND	ND	2.291	2.221	
29,4S,9W	Sensel Spring	Max.	17.1	7.7	456	666	290	29	2	113	13	35	6.5	32	11	TNTC	TNTC	0	BDL	1.42	
		Min.	11.6	6.6	261	602	239	25	BDL	85	11	16	1	29	8.9	0	68	0	BDL	BDL	
		N	26	26	14	26	26	26	26	26	26	25	26	26	26	26	10	10	2	26	26
		Avg.	13.98	7.227	408.7	631.8	267.8	26.32	0.50	103.2	11.6	31.2	5.16	30.4	9.70	ND	ND	ND	BDL	0.153	
		Std.	1.065	0.235	43.34	13.82	18.26	0.983	0.470	6.674	0.756	4.877	1.061	0.781	0.478	ND	ND	ND	ND	0.306	
4,4S,9W	Walsh Spring	Max.	16.5	8.3	371	758	304	26	9	96	24	17	30	84	16	4100	4500	2400	1.98	55	
		Min.	9.3	7.1	365	301	112	8.7	2	39	8.0	9.4	1.8	25	6.7	0	860	40	0.16	0.38	
		N	12	12	2	12	12	12	12	12	12	12	12	12	12	12	1	2	2	12	12
		Avg.	14.60	7.592	368.0	438.3	170.1	14.6	4.58	60.6	13.1	13.9	5.15	49.0	10.7	ND	ND	ND	0.886	7.305	
		Std.	1.856	0.324	ND	132.7	55.75	4.863	1.705	16.61	4.799	2.137	7.597	20.81	2.522	ND	ND	ND	0.618	14.97	
29,3S,9W	Kelly Spring and Big Sink	Max.	18.2	8.5	470	782	298	50	8	97	48	17	7.36	116	25	TNTC	TNTC	1300	16	98	
		Min.	7.0	7.0	248	169	40	7.0	2	22	4.7	7.0	0.6	15	4.5	6000	590	178	BDL	BDL	
		N	33	33	18	33	33	33	33	33	33	33	31	33	33	33	7	8	2	33	33
		Avg.	14.61	7.594	394.1	456.9	157.1	24.5	4.30	54.3	14.3	10.9	4.34	47.6	14.7	ND	ND	ND	5.181	25.6	
		Std.	2.417	0.428	47.1	206.6	94.44	14.74	1.714	25.59	9.301	3.203	2.085	26.46	5.07	ND	ND	ND	5.942	33.0	
31,3S,9W	Illinois Caverns	Max.	14.5	8.0	458	572	248	22	2	94	12	22	6.44	27	16	TNTC	TNTC	68	1.22	1.38	
		Min.	12.6	7.4	262	498	195	15	BDL	72	8.7	19	4.32	22	13	470	300	10	BDL	BDL	
		N	15	15	3	15	15	15	15	15	15	14	15	15	15	15	4	5	3	15	15
		Avg.	13.75	7.718	387.3	546.1	219.4	19.5	0.70	85.6	10.3	20.2	5.43	25.1	14.6	ND	ND	ND	0.213	0.325	
		Std.	0.581	0.236	ND	21.14	14.29	1.667	0.672	4.626	0.728	0.745	0.573	1.258	1.011	ND	ND	ND	0.319	0.328	
Detection limits								1.34	0.629	0.004	0.003	0.050	0.005	0.010	0.010	1	1	1	0.010	0.010	

ND = Not determined

Max = Maximum value

Min = Minimum value

N = Number of analyses

Avg = Arithmetic mean

Std. = Standard deviation. Not determined for N < 5

BDL = Below detection limits

TNTC = Too numerous to count

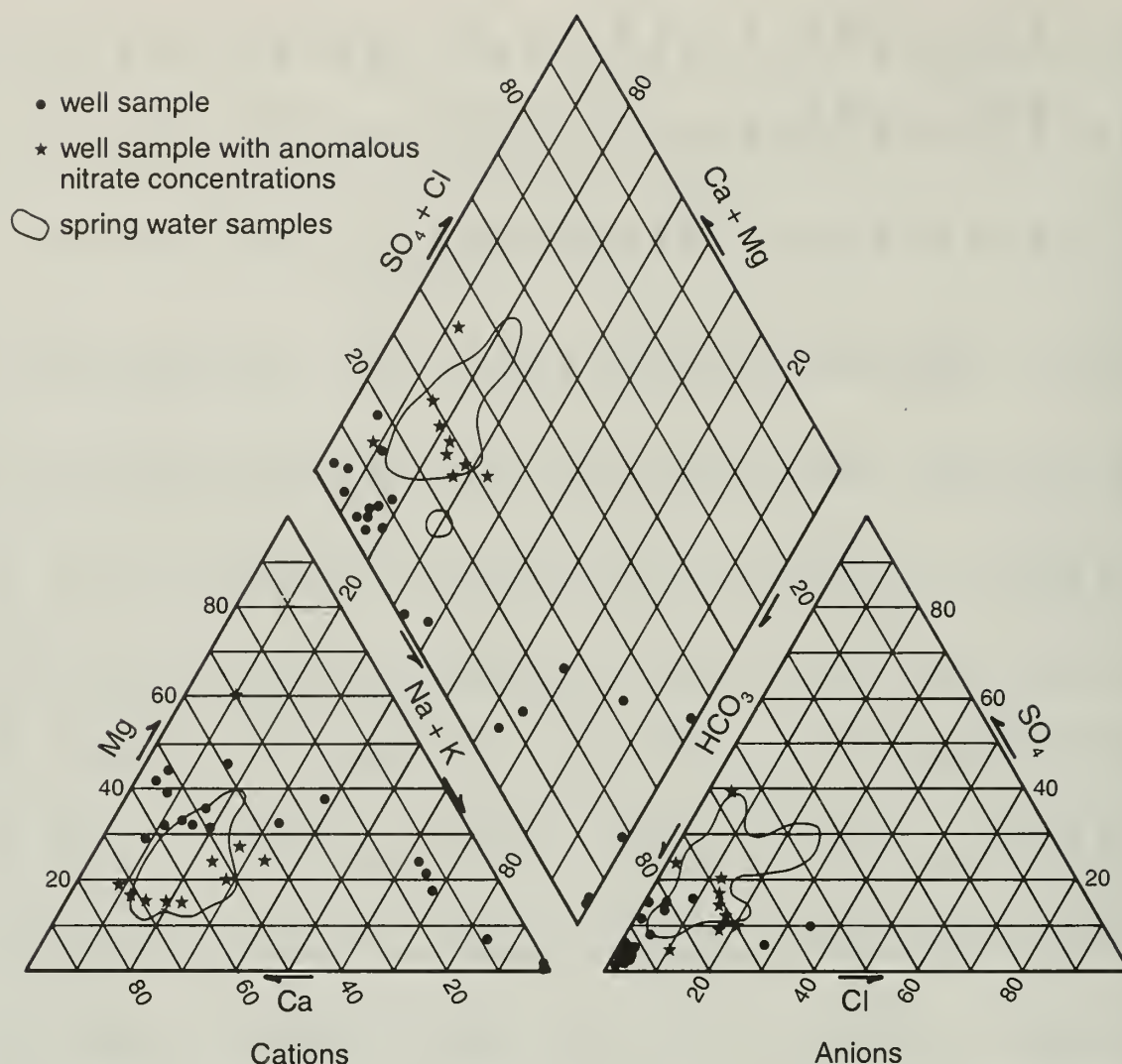


Figure 8 Trilinear diagram of all groundwater samples collected from springs and wells during 1994, 1995, and 1996. Those areas on the diagram occupied by spring water samples are outlined to show relationships with groundwater samples collected from wells.

Alkalinity was calculated from specific conductance measurements for most water samples collected in 1995; alkalinity for water samples from well transects was measured on water samples.

Shuster and White (1971) suggested that the variability in alkalinity concentrations of a series of groundwater samples collected over a period of time can be indicative of the type of groundwater flow system. Water flows rapidly through a conduit flow system comprised of caves and/or large fissures. Water flows more slowly in a diffuse flow system comprised of small fractures, bedding planes, and/or interconnected pore spaces in the rocks. Shuster and White suggested that a coefficient of variation (CV) in alkalinity concentration greater than or equal to 0.10 indicates a conduit flow system, whereas a CV less than 0.10 indicates a diffuse flow system. Of the 10 springs and four wells sampled extensively, eight springs and one well were classified as having conduit flow systems; two springs and three wells were classified as having diffuse flow systems (table 2). On the basis of this classification, all springs and the well in karst terrain exhibited conduit flow, whereas those springs and wells located in nonkarst areas exhibited diffuse flow.

Groundwater Contamination

Bacteria

Springs Each of the water samples collected from springs in karst terrain contained coliforms (including fecal coliform) and enterococci, as well as other aerobic bacteria. All samples exceeded the drinking water standard of less than 1 colony of coliform and fecal coliform bacteria per 100 mL of water (Pontius 1992). The concentrations of bacteria types examined were between 10 colonies/100 mL and TNTC colonies/100 mL (table 1). Because the water samples from springs contained large bacterial concentrations throughout 1994, we collected only a limited number of samples for

Table 2 Coefficient of variation (CV) of alkalinity concentrations for springs and selected wells indicating the type of groundwater flow.

Site name	CV of alkalinity	n	Groundwater flow type	Terrain	Land use
Kelly Spring (K)	0.71	22	Conduit	K	Crops and forest
Boy Scout Spring (BS)	0.52	10	Conduit	K	Forest and crops
Unnamed Spring (U)	0.46	14	Conduit	K	Forest and crops
Big Sink (BK)	0.36	10	Conduit	K	Crops
Walsh Spring (WH)	0.33	12	Conduit	K	Crops and forest
May Spring (M)	0.29	12	Conduit	K	Crops
Illinois Caverns (I)	0.29	13	Conduit	K	Crops
Andys Run Spring (A)	0.28	12	Conduit	K	Urban and crops
Well W (W)	0.17	10	Conduit	K	Urban and crops
Sensel spring (SL)	0.02	26	Diffuse	C	Crops and livestock
Solich spring (SH)	0.01	9	Diffuse	C	Crops and forest
Well B (B)	0.01	7	Diffuse	C	Crops and urban
Well C (C)	0.01	13	Diffuse	C	Crops
Well S (S)	0.01	5	Diffuse	C	Crops and livestock

CV greater than or equal to 0.10 is indicative of conduit flow in a karst aquifer (Shuster and White 1971)

n = number of samples used to calculate CV

C = soil-covered limestone with no karst features observed at the surface

K = karst terrain

bacterial analysis during the second year of this investigation. Spring water samples collected in February 1996 were analyzed for bacterial species and showed a suite of bacterial species typical of the microflora of the intestines of humans and animals (table 3). The concentrations of bacteria in the springs was typically high (TNTC).

Monroe-Randolph Bi-County Health Department well data The MRCHD reported that approximately 67% of all wells sampled in its district were, at some time, contaminated with coliform bacteria (table 4). Analysis of the MRCHD data set indicated that bacterial concentrations in water samples from wells that had been drilled into bedrock exhibited a random spatial distribution that did not appear to be related to the location of sinkholes (fig. 9). Of the wells within or adjacent to (defined as within 1.0 km) karst terrain, 67% contained coliform bacteria; 65% of the wells in the nonkarst terrain also contained coliform bacteria. The similarities in the distribution of wells containing coliform bacteria, regardless of spatial relationship to karst terrain, initially indicated that surface karst features did not have a significant effect on groundwater quality with respect to coliform bacteria. The transect-well data (discussed in the next section) do not, however, support this conclusion.

Table 5 shows the changes in the distribution of wells containing coliform bacteria from 1986 to 1995. Two-year averages of the percentage of MRCHD well water samples containing coliform bacteria indicate that bacterial contamination has increased rapidly since about 1987 (fig. 10). The increase coincides with the increasing population in Monroe County, as reflected by the number of building permits issued per year (table 5). The result of this growth was an increase in the construction of houses, septic systems, and wells in areas dominated by karst terrain and aquifers that may be highly susceptible to groundwater contamination.

Table 3 Bacterial indicators and bacterial genus, and genus and species present in discharge from 10 Monroe County springs in February 1996.

Bacteria	Colonies/100 mL *
Coliform	>200
Fecal coliform	>200
Enterococcus	>200
Total bacteria	>6000
<i>Bacillus asteroides</i>	
<i>Bacillus cereus</i>	
<i>Citrobacter</i> sp.	
<i>Escherichia coli</i>	
<i>Klebsiella pneumoniae</i>	
<i>Pseudomonas aeruginosa</i>	
<i>Pseudomonas</i> sp.	
<i>Streptococcus avium</i>	
<i>Streptococcus faecalis</i>	
<i>Streptococcus faecium</i>	

*The number of colonies for the indicator bacteria were identical for each spring, with the exception of Sensel and Solich Springs, which had fewer bacteria present.

Table 4 Percentage of well samples containing bacteria, nitrate, and/or pesticides; samples collected by the MRCHD during 1991 to 1994, and the ISGS during April, July, and October of 1995 and February 1996.

Source of data	Total bact. ^a	Col. bact. ^b	Fecal col. ^b	Nitrate ^c	Atrazine ^d	Alachlor ^d	n
MRCHD	nd	67%	nd	2.3%	nd	nd	263
ISGS, Apr.	21%	28%	6.9%	6.9%	55%	6.9%	29
ISGS, July	52%	55%	17.0%	3.4%	17%	14%	29
ISGS, Oct.	18%	21%	0%	3.6%	11%	11%	28
ISGS, Feb	29%	21%	7.1%	3.6%	14%	14%	28

^aall bacterial counts other than coliform or fecal coliform that were 80 colonies/100 mL water

^bcoliform and fecal coliform bacteria counts greater than or equal to 1 colony/100 mL water

^cnitrate concentrations greater than 10 mg/L (as N)

^dpesticide concentrations greater than 0.01 µg/L

n = number of wells

nd = not determined

Table 5 Summary of water quality data for Monroe County wells from the files of the MRCHD from 1986 to 1995 showing the number and proportion of wells tested and found to contain coliform bacteria and NO₃⁻ concentrations exceeding the U.S. EPA regulatory limit, and the number of building permits issued by the Monroe County zoning office.

Year	Total number samples	Samples containing coliform	Samples containing nitrate	Percentage with coliform	Percentage with nitrate ^a	Coliform two-year average	Building permits issued ^b
1986	255	93	15	36.5	5.88		79
1987	276	69	12	25.0	5.35	30.7	92
1988	279	157	30	56.3	10.80		82
1989	304	155	23	51.0	7.57	53.6	95
1990	480	269	34	56.0	7.08		80
1991	398	258	10	64.8	2.51	60.4	66
1992	335	195	15	58.2	4.48		110
1993	308	209	4	67.9	1.30	63.0	143
1994	354	251	15	70.9	4.24		163
1995	264	144	20	54.5	7.58	62.7	98

^anitrate concentrations ≥10 mg/L as N

^bfor residential dwelling units. The mean number of permits issued per year from 1980 through 1985 is 55.8.

Many of the houses were built as multiple house developments in wooded areas not used as croplands, in part, because of the abundance of sinkholes. The clustering of new houses in karst terrains may explain the rapid increase in the number of contaminated wells.

Transect wells Bacterial concentrations in groundwater samples collected during our investigation (fig. 11) indicated a relationship between well location and the presence of coliform bacteria in groundwater of karst terrain. Of the 20 wells within or adjacent to (within 1.0 km) karst terrain, 75% contained coliform bacteria. Only 44% (n = 9) of the wells within nonkarst terrain contained coliform bacteria, indicating a higher incidence of bacterial contamination in wells near karst terrain. The bacterial species found in the transect wells (table 6) are consistent with those normally found in human and animal wastes.

Our data indicate that 62% of the transect wells tested positive for coliform bacteria at some time during the four-season sampling period. This result is comparable with the 67% of the sampled wells that tested positive for coliform bacteria from the MRCHD files (table 4). Bacteria were, however, detected in more than twice as many wells along the transect in July as compared with the other three sampling periods (fig. 11). Bacterial concentrations probably increased in shallow karst

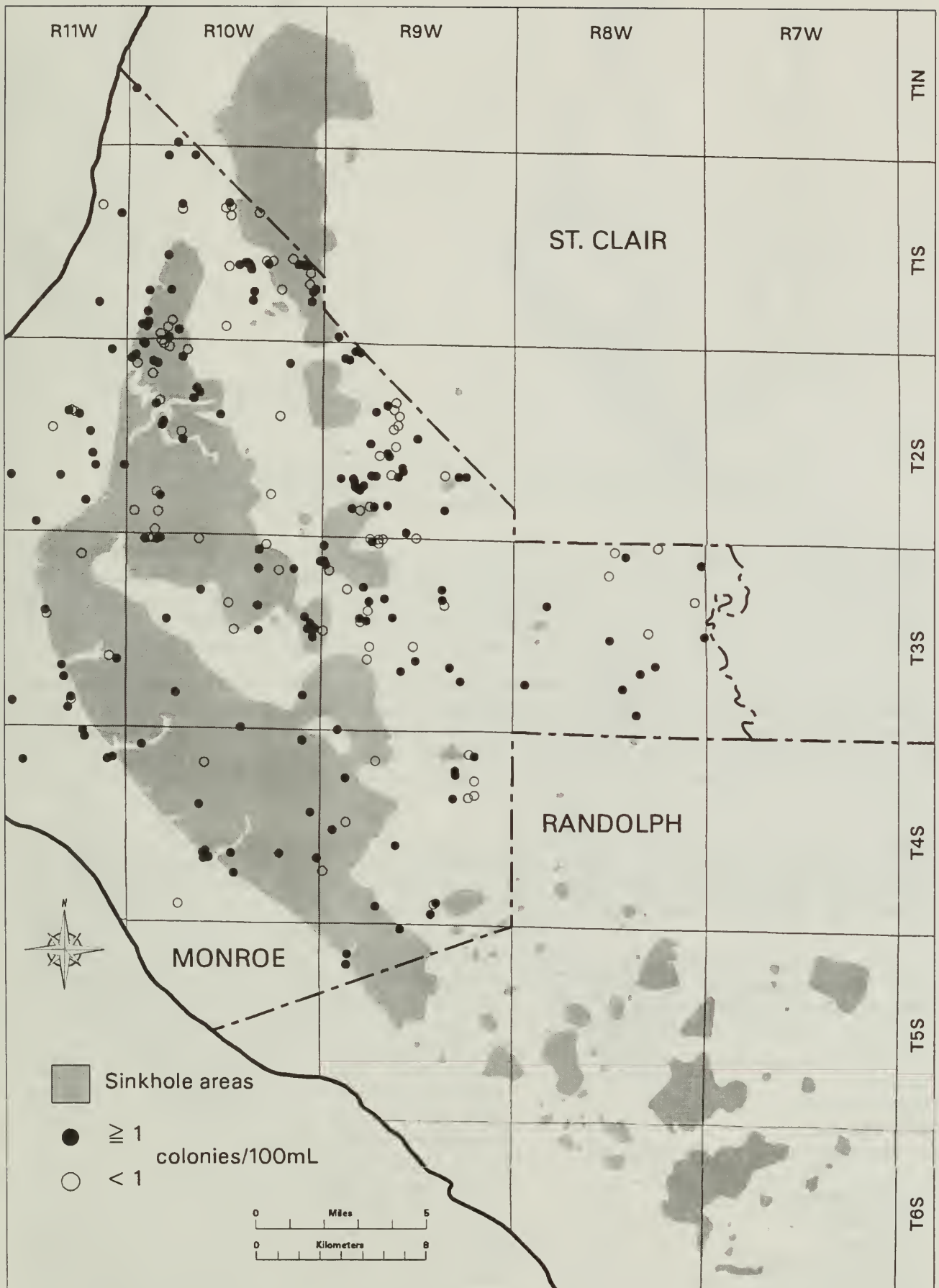


Figure 9 Distribution of private wells having water that contained coliform bacteria (as colonies per 100 mL of water). Groundwater samples were from 263 wells drilled in bedrock in Monroe County. Well location and analytical data were collected from the files of the MRCHD.

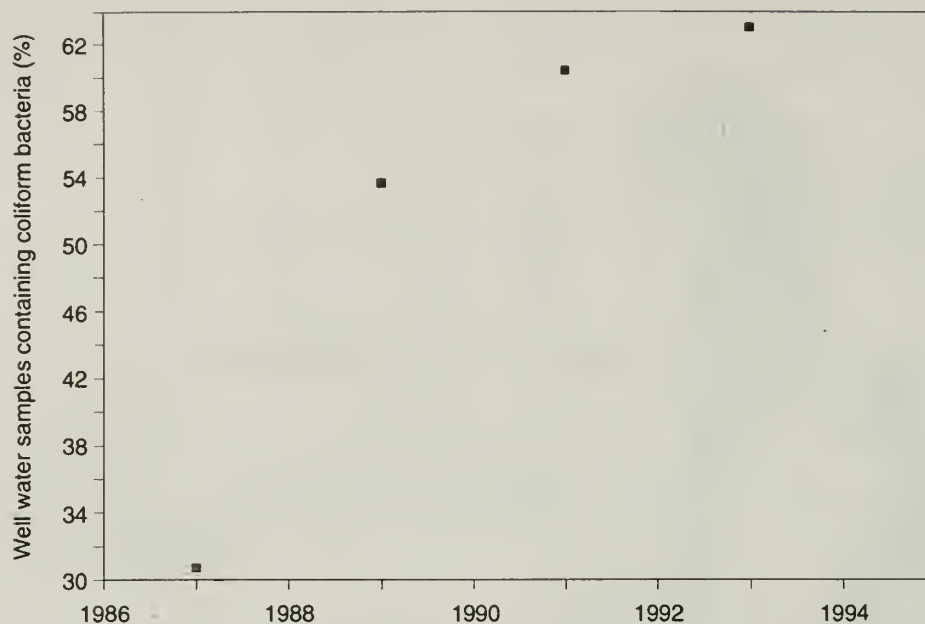


Figure 10 Percentage of well water samples containing coliform bacteria in Monroe County (two-year averages). The rapid increase coincides with higher rates of residential development that began in the county in about 1987.

aquifers during the summer months when higher soil and water temperatures were conducive to bacterial growth. Bacteria colonies, including coliform bacteria, typically decrease in surface and soil waters during the colder months, especially after the first freeze of the season (E.C. Storment, Illinois Dept. of Agriculture Animal Disease Lab., personal communication, 1995). In general, the wells most affected by seasonal bacterial concentrations were those in and adjacent to karst terrain.

Source(s) of bacteria Field observations suggest that effluent from livestock wastes and private septic systems were the two major sources of bacteria in groundwater samples from the study area. In several areas, cattle and other livestock grazed at or were confined to areas immediately adjacent to wells and sinkholes; some cattle had access to streams that discharged into swallow holes. In addition, manure was used as organic fertilizer on some croplands where numerous sinkholes were present.

Septic effluent appears to be a widespread and potentially more serious problem than livestock waste. The failure of septic systems to perform as designed is well known in midwestern states. As many as 50% of the septic systems in Illinois are reported to perform below minimum standards (Kiker 1958, Aley and Thomson 1984, Bigari 1994). Missouri and Minnesota have failure rates of 60% and 70%, respectively. Ideally, the filtering capabilities and biological activity of soils will remove the pathogens present in septic effluent before they enter shallow aquifers, provided the regolith is thick enough to accommodate a leach field (Zoeteman 1985). Macropores typically present in regolith in karst terrain may, however, shortcut the effluent treatment process, resulting in a septic system that acts as a point source for bacterial contamination (Wells and Krothe 1989, Ferguson et al. 1991). Extreme cases of this type of problem were often observed where private, aeration-type septic systems discharged effluent directly into sinkholes. This practice was common in the study area prior to 1988, and most of those systems are still in operation. Discharge of septic systems to sinkholes was prohibited after 1987, and septic systems are now required to discharge to leach fields or onto level ground. However, exceptions to this requirement continue to be granted in the study area.

Table 6 Bacterial indicators and bacterial genus, and genus and species present in transect wells during February 1996.

Bacteria	Wells (%)
Coliform	26.0
Fecal coliform	7.4
Enterococcus	8.5
Total bacteria >80 colonies/100 mL	26.0
<i>Pseudomonas</i> sp.	37.0
<i>Escherichia coli</i>	18.5
<i>Bacillus</i> sp.	14.8
<i>Streptococcus faecalis</i>	14.8
<i>Aeromonas</i> sp.	7.4
<i>Klebsiella ozonae</i>	7.4
<i>Pseudomonas cepacia</i>	3.7
<i>Streptococcus faecium</i>	3.7

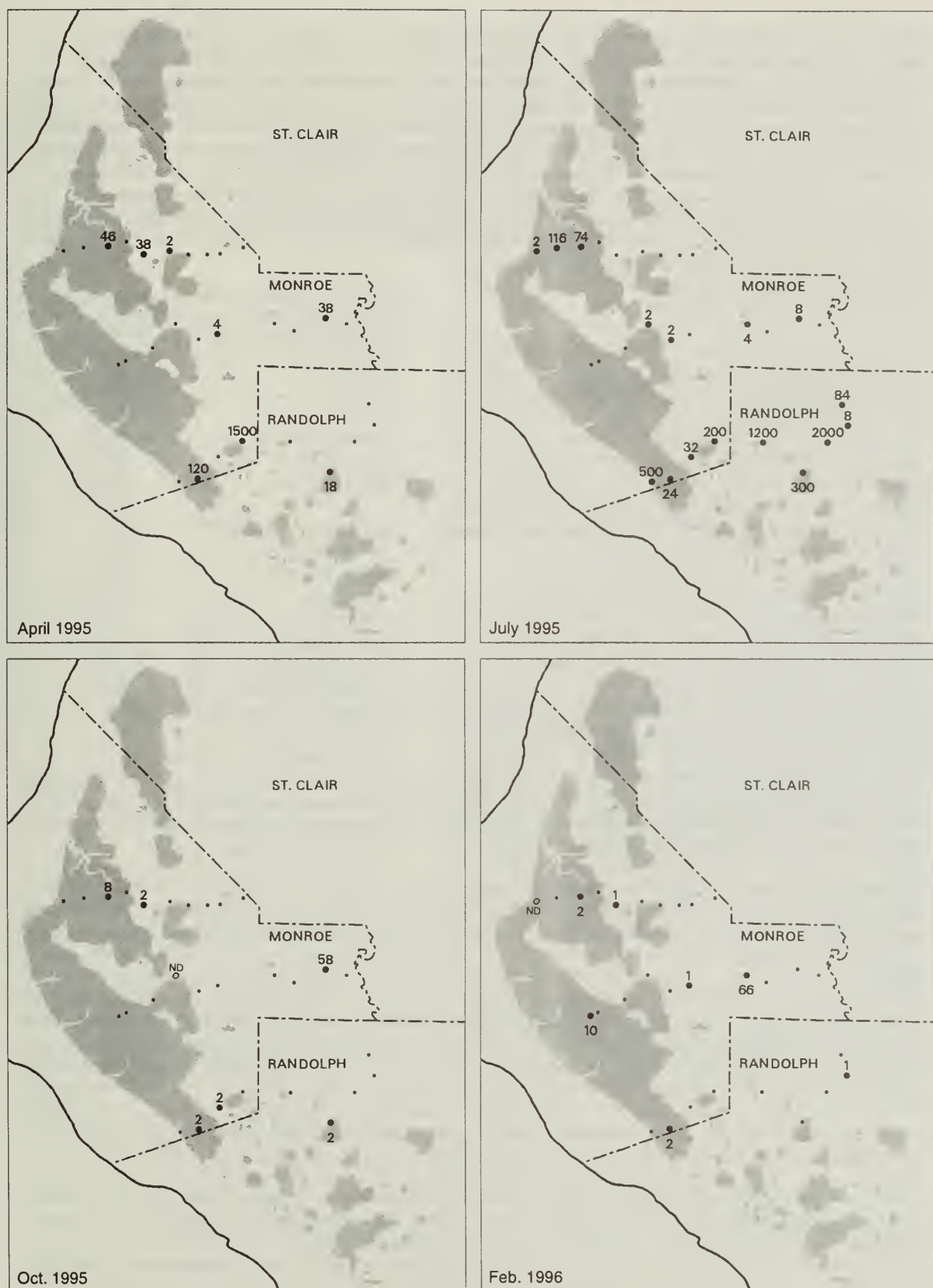


Figure 11 Distribution of wells containing coliform bacteria (as colonies per 100 mL of water) in ground-water samples. Data are from wells along three transects in April 1995, July 1995, October 1995, and February 1996. ND = no data.

Samples of discharge from three different types of septic systems were collected from private residences and analyzed for bacterial content as a preliminary test of the quality of water being discharged into the shallow karst aquifer via sinkholes. The samples were collected from a buried sand filter, an aeration system, and a combined aeration system and leach field. Each system was less than 10 years old. Discharge from these systems is typically allowed to run out onto the ground, into small streams, and directly into sinkholes. Bacteria present at high concentrations in the effluent included the indicator bacteria coliforms, fecal coliform, enterococcus (200 colonies/100 mL), and a total aerobic plate count greater than 6,000 colonies/100 mL. Bacterial species present in the effluent are listed in table 7. If the bacteria-laden waters discharging from the three selected septic systems are representative of the effectiveness of these systems and if 50% to 70% are expected to fail, it is likely that private septic systems are a significant source of the bacterial contamination found in southwestern Illinois.

The potential for fecal material in shallow karst aquifers to discharge into karst springs and to be pumped from wells appears to be high in this region. Spring waters could be a health hazard to those who drink or even come in contact with the water because water contaminated with human wastes may be contaminated with viruses that can be transmitted by ingestion or through contact with an open wound (E.C. Stormont, Illinois Dept. of Agriculture Animal Disease Lab., personal communication, 1995).

The bacteria identified in the springs, transect wells, and septic systems (tables 3, 6, 7) are enteric and, as such, part of the normal microflora of the intestines of humans and animals. Many of these bacteria are feebly to significantly pathogenic to humans. Most of the bacteria are opportunistic, causing infections in those who are already in a weakened state, such as the elderly and the debilitated (Freeman 1985). Others are pathogenic to aquatic creatures, including cold-blooded vertebrates (Freeman 1985) that inhabit the study area. Several of the bacterial species present in the drilled wells are capable of causing a variety of gastrointestinal and other infections (Cason et al. 1991). Bacteria and associated viruses entering shallow karst aquifers and springs ultimately are discharged into surface waters, thereby leading to the degradation of surface streams in this area and areas downstream.

Nitrate

Nitrate is a negatively charged ion derived from natural and anthropogenic sources, including mineralization of natural organic nitrogen, fertilizer, livestock, and private septic systems. The processes of ammonification and nitrification can occur in the soil zone above the water table when N in organic matter is converted via microbial activity to ammonium (NH_4^+) and subsequently oxidized to NO_3^- (Freeze and Cherry 1979). Because it is a positively charged ion, NH_4^+ is readily adsorbed by negatively charged soil components. Nitrate, being negatively charged, is not significantly adsorbed by soil components. It can thus migrate downward through the regolith with infiltrating rain water or snowmelt and enter shallow aquifer systems (Burt et al. 1993).

A natural background concentration of NO_3^- (as N) in groundwater samples collected from springs and wells in the study area was calculated to be 1.4 mg/L on the basis of a graphical determination using a cumulative probability technique developed by Sinclair (1974). Concentrations of NO_3^- (as N) less than 1.4 mg/L were assumed to be naturally occurring; those at and greater than this threshold were anomalous and assumed to be anthropogenic in origin. Kolpin et al. (1994), using another technique for data analysis, calculated a similar threshold value (3.0 mg/L) for groundwater of the midcontinental United States.

Springs Nitrate in groundwater samples collected at springs was detected in concentrations ranging from less than 0.10 to 30 mg/L. The mean NO_3^- concentration for spring samples was

Table 7 Bacterial indicators and bacterial genus, and genus and species present in discharge from three septic systems.

Bacteria	Colonies/100 mL
Coliform	>200
Fecal coliform	>200
Enterococcus	>200
Total bacteria	>6000
<i>Aeromonas hydrophilia</i>	
<i>Aeromonas</i> sp.	
<i>Bacillus cereus</i>	
<i>Bacillus</i> sp.	
<i>Citrobacter freundii</i>	
<i>Citrobacter</i> sp.	
<i>Escherichia coli</i>	
<i>Klebsiella ozonae</i>	
<i>Klebsiella pneumoniae</i>	
<i>Proteus mirabilis</i>	
<i>Pseudomonas aeruginosa</i>	
<i>Pseudomonas</i> sp.	
<i>Staphylococcus aureus</i>	
<i>Streptococcus faecalis</i>	
<i>Streptococcus faecium</i>	

4.7 mg/L, and 92% of all spring water samples exceeded background concentrations. The U.S. EPA regulatory limit of 10 mg/L for NO_3^- (as N) was equaled or exceeded only in two water samples collected from springs during this investigation. For comparison, Rowden et al. (1993) found NO_3^- (as N) concentrations ranged from 6.8 to 17 mg/L during water year 1991 (October 1990 to September 1991) in water samples from Big Spring, a large spring draining a karst region in northeastern Iowa. The authors stated that the total loading of agrichemicals in the spring was a function of climatic variations that included timing and intensity of snowmelt and precipitation.

Nitrate concentrations in water samples from Monroe County springs were generally greater than those from wells (discussed below). Approximately 75% of the well samples contained NO_3^-

concentrations less than 1 mg/L, whereas approximately 90% of the spring samples contained NO_3^- concentrations between 1 and 10 mg/L (fig. 12).

Monroe-Randolph Bi-County Health Department well data Nitrate concentrations present in well water samples collected in Monroe County by the MRCHD (fig. 13) had a mean value of 3.64 mg/L, a standard deviation of 3.35 mg/L, and a range of 0 and 31 mg/L. The percentage of wells that contained NO_3^- concentrations of greater than 10 mg/L during each of the last 10 years ranged from 1.30% to 10.8%, with no apparent annual trend (table 5). The distribution of concentrations shown in figure 13 suggests that wells containing the largest concentrations of NO_3^- (10 mg/L) were located at or near the margins of karst terrain (within 1.0 km) and near the base of the Mississippi River bluff, especially where surface streams drain the highlands.

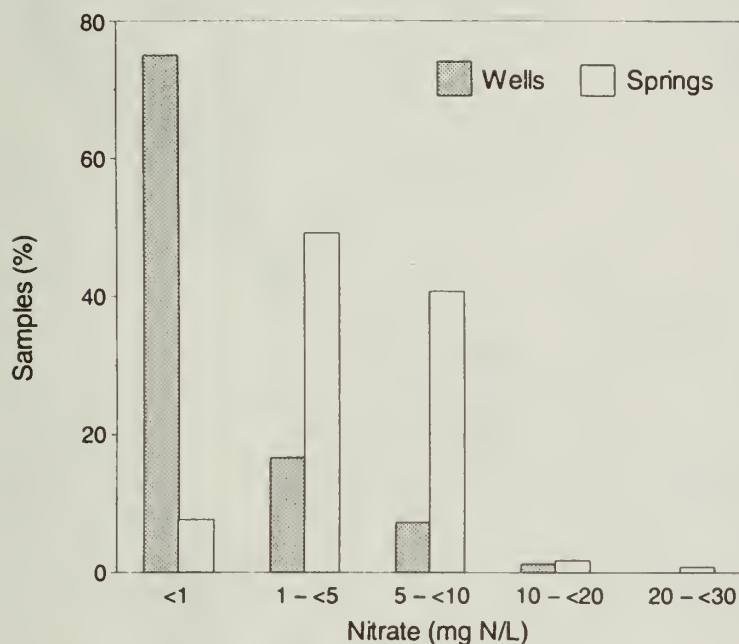


Figure 12 Frequency distribution of NO_3^- (as N) concentrations in groundwater samples from all springs and wells. Larger nitrate concentrations were present in samples from springs.

Transect wells Well-defined temporal changes in NO_3^- concentrations were not evident in the data collected along the three well transects (fig. 14). In general, NO_3^- concentrations changed little throughout the sampling period, a finding that is consistent with MRCHD long-term water quality data discussed previously. The occurrence of elevated NO_3^- concentrations with respect to location of karst terrain was consistent with that observed in the MRCHD data (fig. 13). Of the 13 wells containing concentrations of $\text{NO}_3^- \geq 6$ mg/L, 11 (85%) were located at or near karst margins. We speculate that surface waters draining into the Mississippi valley from the highlands were responsible for the enrichment of NO_3^- along the base of the bluff. The reason for the enrichment of NO_3^- in groundwater near karst margins on the highlands was less clear and is under investigation by the authors.

Of the transect wells, 31% contained NO_3^- concentrations greater than the threshold concentration of 1.4 mg/L, 6.9% contained NO_3^- concentrations greater than or equal to 10 mg/L in April, and about 3.5% had such high concentrations in July, October, and February. The highest NO_3^- concentration (19.6 mg/L) occurred in well 4C (appendix: table A1), which was located in close proximity to a dairy farm. This well was also severely contaminated with coliform and fecal coliform bacteria. Nitrate concentrations in well 4C decreased to background levels in July and October, while bacteria concentrations were greatest in the July water sample.

The plot of water quality data for samples from all wells with anomalously large NO_3^- concentrations tended to overlap the area defined by the spring water samples (except for one, which was not in a karst area; fig. 8). The chemical similarity between groundwater from the wells and springs suggested that water samples collected from the wells were predominantly from shallow karst aquifers. These data suggest that the presence of NO_3^- in the wells may have resulted from well

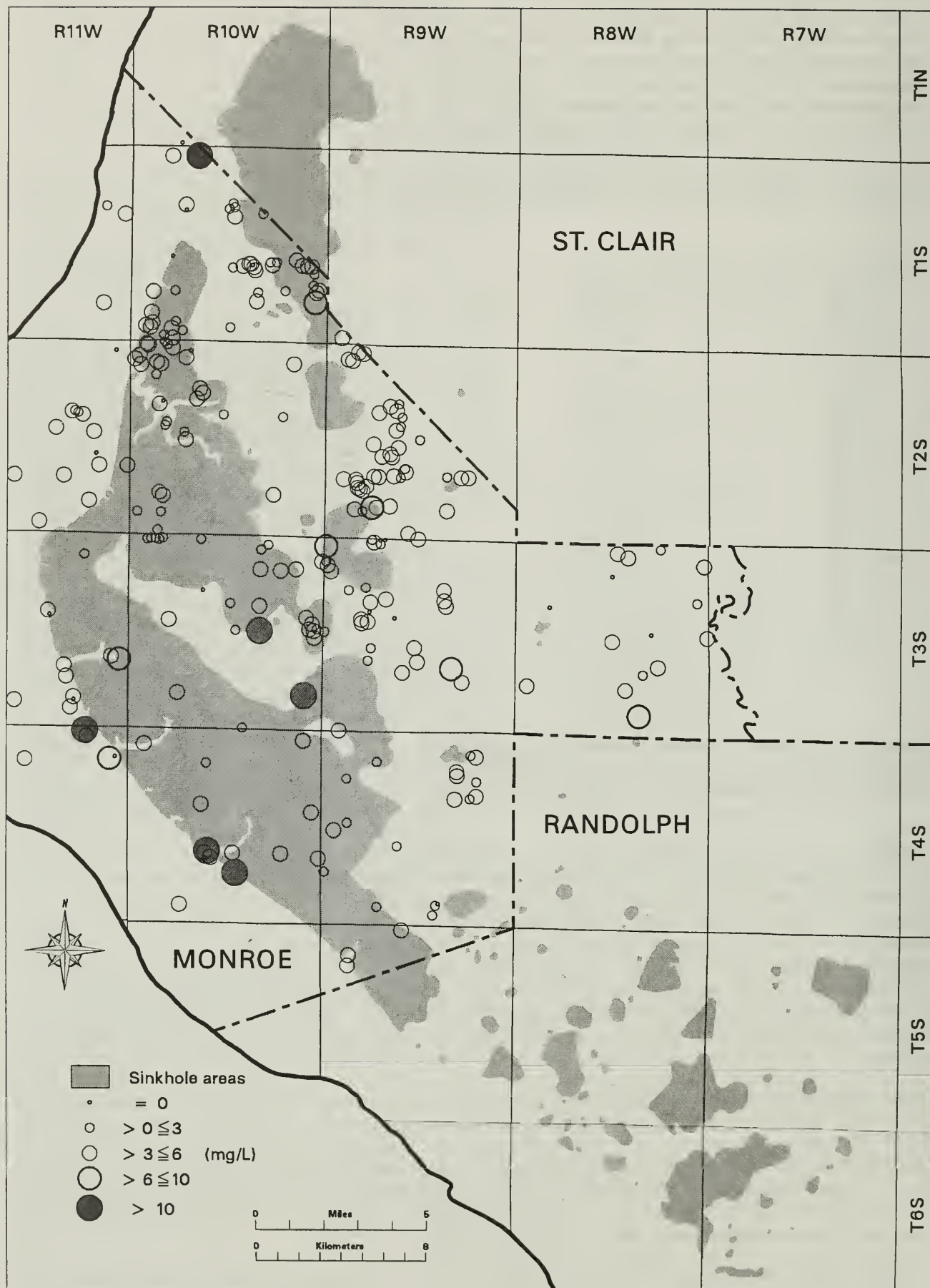


Figure 13 Distribution of NO_3^- (as N in mg/L) present in groundwater samples taken in 1991–1994 from 263 wells drilled in bedrock in Monroe County. Well location and analytical data were collected from the files of the MRCHD.

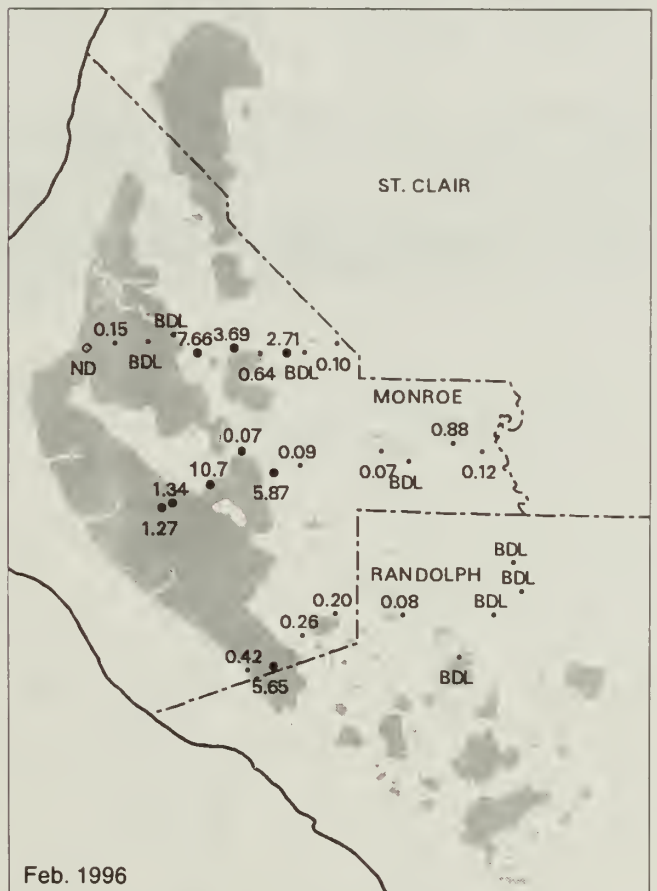
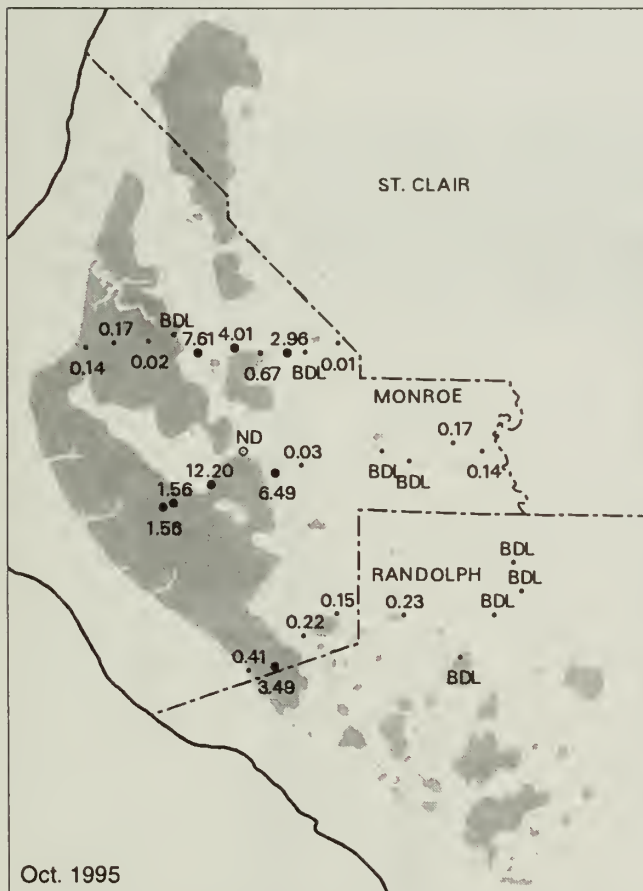
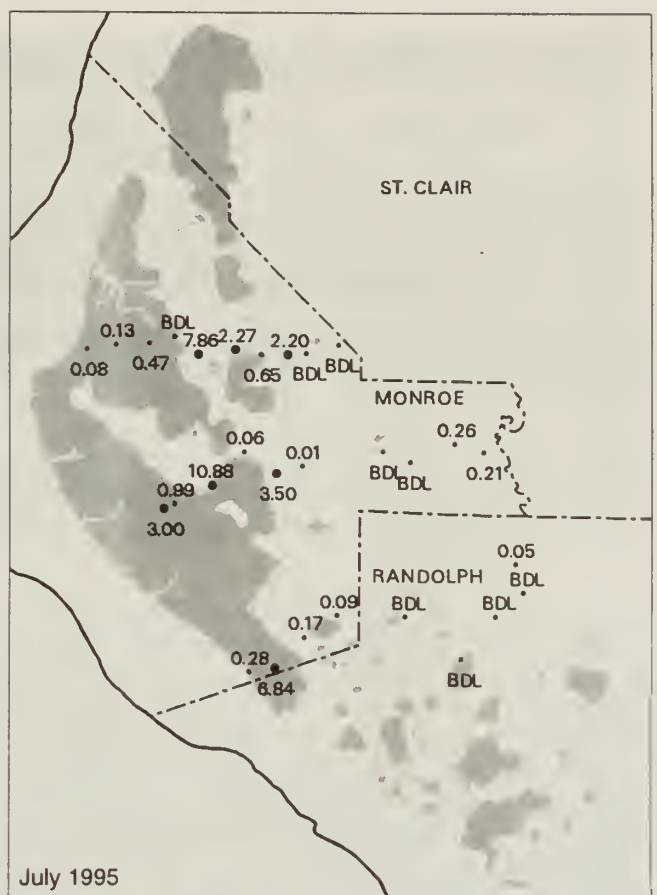
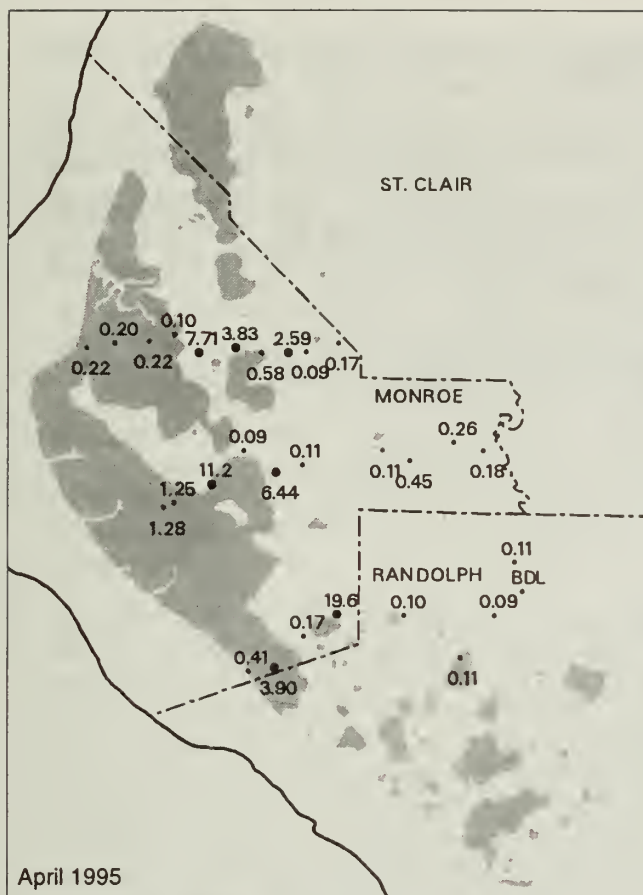
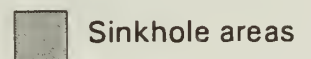
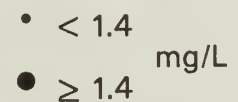
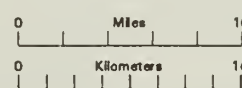


Figure 14 Distribution of NO_3^- (as N in mg/L) concentrations in groundwater samples. Data are from wells along three transects in April 1995, July 1995, October 1995, and February 1996. BDL = below detection limits; ND = no data.



construction techniques that do not adequately prevent contaminants in the shallow karst aquifer from entering wells that have been drilled to greater depths.

There was no correlation between NO_3^- concentrations and well depths shallower than 110 m (360 ft; fig. 15), a result contrary to what Glanville (1985) found in the Big Spring basin of Iowa. Glanville found a gradational decrease in NO_3^- concentrations with increasing depth (to 75 m [250 ft] deep) in both karst terrain and in covered karst terrain where overlying regolith was less than 15 m (50 ft) thick. The very small NO_3^- concentrations below 110 m (fig. 15) were probably the result of denitrification in the anaerobic environments of the deeper wells.

Results of a study of agrichemical contamination in rural private wells in Illinois (Schock et al. 1992, Mehnert et al. 1995) revealed that NO_3^- was the most frequently detected agrichemical. It occurred

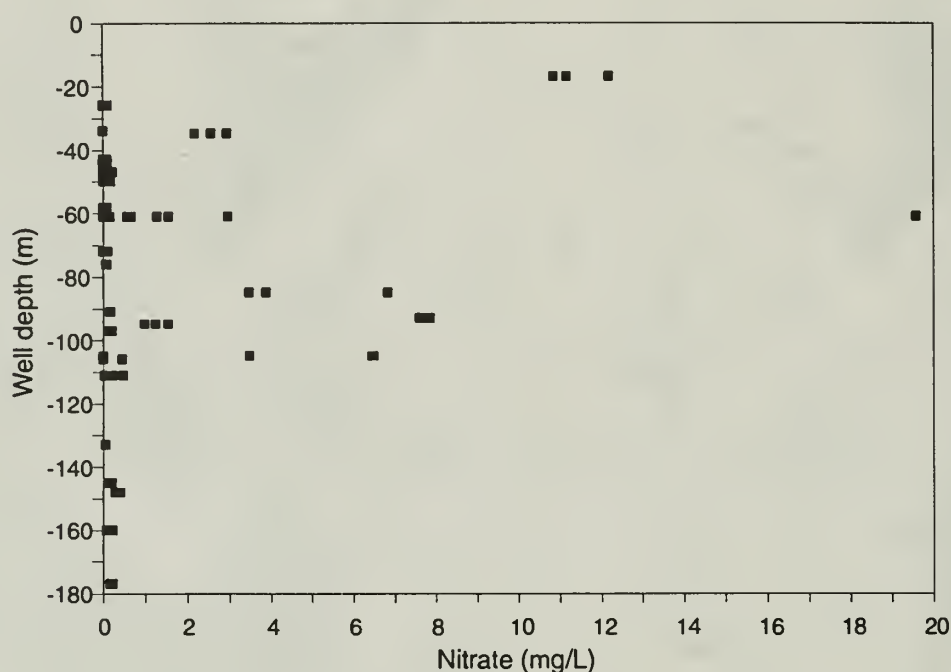


Figure 15 Well depth versus NO_3^- (as N) concentrations from groundwater samples from transect wells collected in 1995 and 1996.

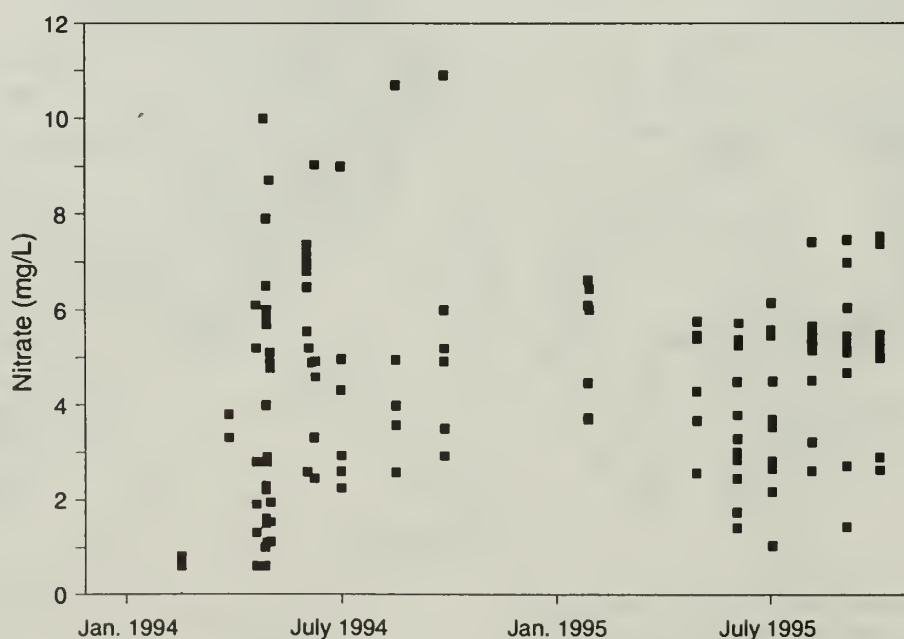


Figure 16 Relationship between NO_3^- (as N) concentrations and sampling date for all groundwater samples collected from springs.

in 42 (18%) of 240 water samples. The greatest NO_3^- concentration found in these studies was 58 mg/L. Anomalous high concentrations of NO_3^- greater than or equal to 3.0 mg/L were detected in 29% of 303 shallow wells tested by the USGS in 12 midcontinent states, including Illinois; NO_3^- concentrations exceeded 10 mg/L in 6% of the wells tested (Kolpin et al. 1994).

Source(s) of nitrate The spotty distribution of elevated concentrations of NO_3^- in wells, and the juxtaposition of wells containing elevated and background concentrations of NO_3^- among wells from the MRCHD data set and our well transects, suggests point-source contamination or possibly a regional source obscured by the vagaries of well construction in karst aquifers. Point sources include private septic systems, which are known to have a high failure rate (Kiker 1958, Aley and Thomson 1984, Bigari 1994), and livestock. Both of these sources are common in Monroe and Randolph Counties. Most of the wells with elevated concentrations of NO_3^- from the MRCHD database (92%) also contained coliform bacteria (fig. 13), and 77% of the wells had concentrations of coliform bacteria that were too numerous to count (200 colonies/100 mL). Effluent from several septic systems allowed to discharge into sinkholes contained NO_3^- concentrations as high as 29 mg/L and NH_3 concentrations as high as 43 mg/L (Panno et al., Illinois State Geological Survey, unpublished data).

Chloride and specific conductance are indicators of changes in the percentage of groundwater entering a spring relative to runoff of rainwater and snowmelt, and NO_3^- was found to behave in a similar manner. Water samples from springs where grab and long-term samples were collected typically showed distinct seasonal changes in NO_3^- concentrations that could be attributed to dilution alone. There was, however, no easily identifiable relationship between the time when N-fertilizers were applied to croplands and the occurrence of elevated concentrations of NO_3^- in spring water (fig. 16) or well water samples when examined collectively. The pattern that did emerge was that the greatest range of NO_3^- concentrations in spring-water samples occurred around the time of spring planting, which is also the time of most abundant rainfall in the study area. Given the available data, it was apparent that NO_3^- was added to the shallow karst aquifer from multiple sources. It was not possible, however, to definitively identify the dominant source of NO_3^- in spring water samples.

Pesticides

Springs Alachlor and/or atrazine were detected in 83% of the groundwater samples collected from springs in the study area (table 1). Pesticide concentrations ranged from 0.10 to 98 $\mu\text{g/L}$ for the spring samples, whereas concentrations in most well samples ranged from ≤ 0.5 to 1.6 $\mu\text{g/L}$ (fig. 17). The U.S. EPA's Maximum Contaminant Level (MCL) for alachlor and atrazine is 2 $\mu\text{g/L}$ and 3 $\mu\text{g/L}$, respectively (U.S. EPA 1991). Atrazine was detected more often and at greater concentrations than alachlor in both wells and springs. The largest concentrations of these pesticides occurred in late spring and early summer of 1994 and 1995 (fig. 18).

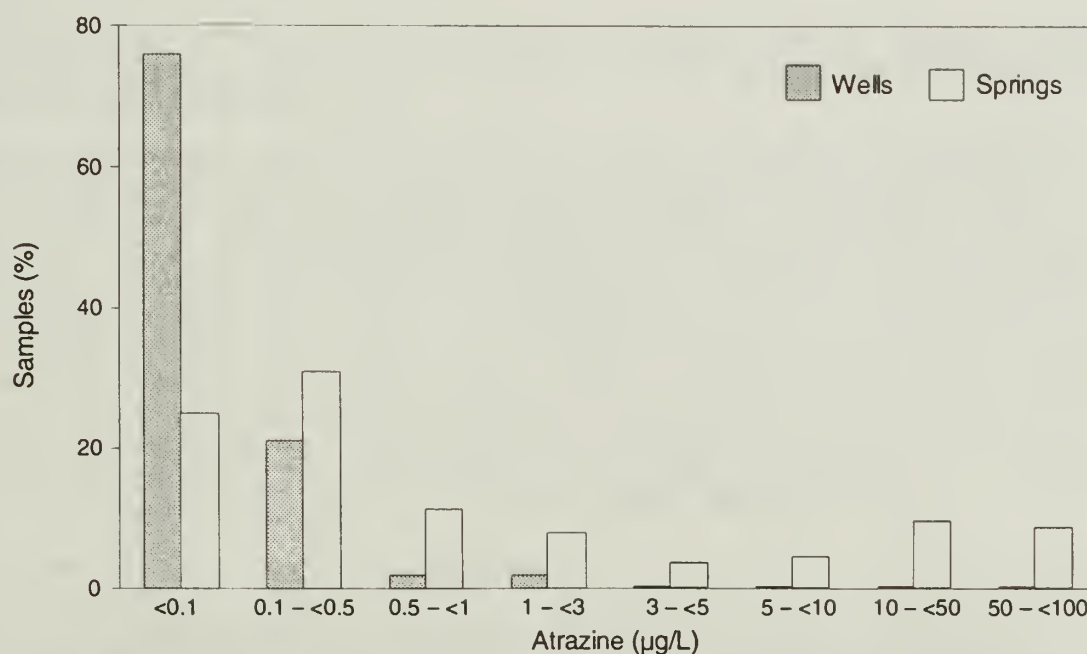


Figure 17 Frequency distribution of atrazine concentrations in groundwater samples from all springs and wells. Larger atrazine concentrations were present in samples from springs.

As a comparison, long-term sampling (since 1981) of groundwater from the Big Spring Basin, a karst region in northeastern Iowa, revealed that atrazine was the most “consistently detected herbicide in Big Spring groundwater” (Rowden et al. 1993). Rowden et al. also found that atrazine concentrations in 1991 ranged from approximately 0.1 to 20 µg/L. Additional herbicides detected included alachlor, cyanazine, and metolachlor.

A plot of atrazine versus NO_3^- concentrations for all spring-water samples in our investigation (fig. 19) revealed two distinct groups: one that contained concentrations of atrazine ranging from 7 to 98 µg/L and one that ranged from <7 µg/L to below detection limits. The group with the largest atrazine concentrations included water samples collected during and following rainfall when surface runoff from croplands occurred. The linear relationship between atrazine and NO_3^- concentrations for this

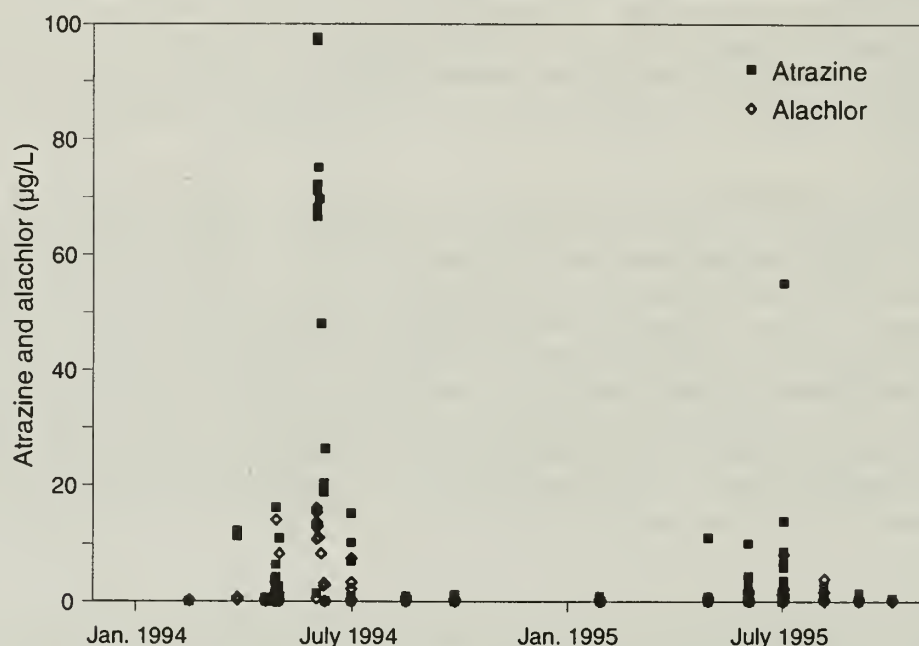


Figure 18 Relationship between concentrations of atrazine and alachlor present in groundwater samples from springs and date of sample collection.

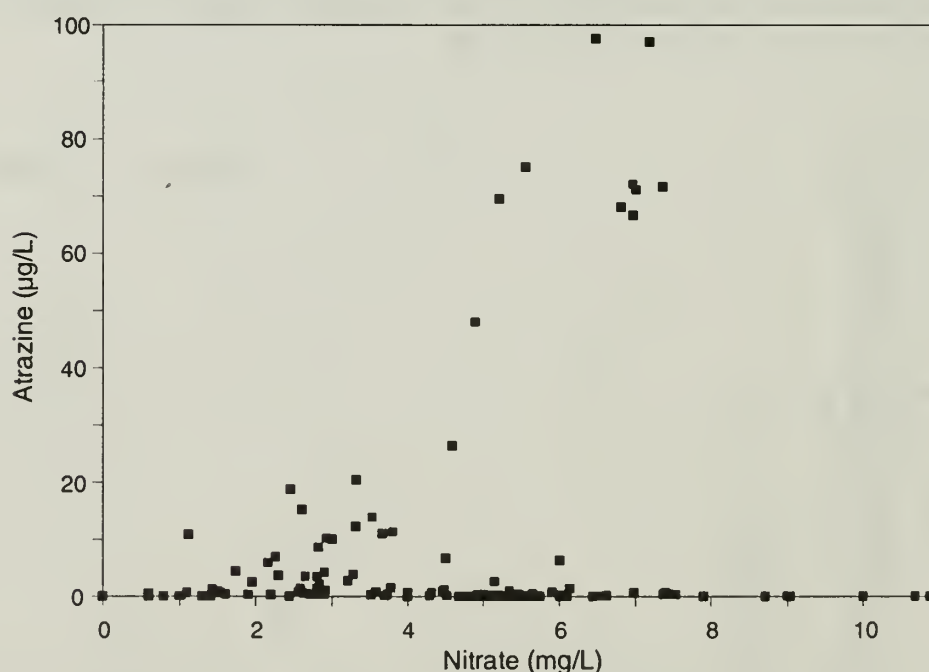


Figure 19 Scatter plot of atrazine versus NO_3^- (as N) concentrations showing two groups: one with large atrazine concentrations that covaried with nitrate and one with atrazine concentrations at or below detection limits but relatively large concentrations of nitrate.

group ($r^2 = 0.80$ for all samples with atrazine concentrations above $7 \mu\text{g/L}$) indicates that these chemicals migrated together into the shallow karst aquifers and exited at the springs. Determining the mechanism by which atrazine moved was beyond the scope of this investigation, but the atrazine and NO_3^- were probably carried in surface runoff from croplands via sinkholes and other conduits as well as by leaching and transport on soil particles. The other group (atrazine $<7 \mu\text{g/L}$ to below detection limits) mostly consisted of water samples collected when springs were at or near base levels. No discernible relationship between atrazine and NO_3^- was observed for this latter group.

Wells Alachlor and/or atrazine were detected in 30% of all water samples collected from the 33 wells in the study area (detection limit = $0.10 \mu\text{g/L}$). Pesticide concentrations in these samples did not exceed drinking water standards (table 8). These data indicate that pesticides had entered the groundwater flow systems of the wells in both karst and nonkarst terrains but were not currently present at concentrations that pose a threat to human health.

The occurrence of pesticides in the transect wells was plotted in relation to time of sampling and spatial relationship to karst features (fig. 20). For figure 20, the concentrations of atrazine and alachlor in each water sample were added together to simplify presentation of the data and so we could generalize about the occurrence of pesticides in the transect wells and the seasonal variability of pesticide concentrations in well samples. Actual concentrations are presented in table 8. Concentrations of atrazine in well water samples were dramatically higher in April than they were in July, October, and February, when both pesticides were commonly below detection limits. Pesticides were detected in 55% of the wells in April, immediately following their application to croplands. Groundwater samples collected during July, October, and February indicated that only 21%, 18%, and 21% of the wells contained detectable pesticide concentrations, respectively (table 8). A similar decrease in the occurrence and concentration of the pesticides in relation to application time was reported by Kolpin et al. (1994). They also found that no groundwater samples from wells contained pesticide concentrations greater than the U.S. EPA MCL for drinking water. The greatest concentration of any pesticide found by Kolpin et al. (1994) was $2.32 \mu\text{g/L}$. Schock et al. (1992) and Mehnert et al. (1995) collected groundwater samples from 240 wells in Illinois and analyzed them for 33 pesticides. Less than 1% of the wells contained atrazine at concentrations in excess of the U.S. EPA MCL; the greatest atrazine concentration found during their study was $3.8 \mu\text{g/L}$.

SUMMARY AND CONCLUSIONS

Nine springs, one cave stream (referred to as a spring herein), and 33 private wells were sampled during 1994, 1995, and 1996. Twenty-nine of the private wells were selected at equally spaced locations along three east–west transects on the highlands of Monroe and Randolph Counties. Water quality data from private wells collected from 1986 to 1995 by the MRCHD also were examined for spatial and temporal trends.

The springs contained large concentrations of coliform bacteria (>200 colonies/100 mL of water) as well as anomalously large NO_3^- concentrations ($\geq 1.4 \text{ mg/L NO}_3^-$ [as N]), and alachlor and atrazine were also frequently detected.

Coliform, fecal coliform, and other bacteria were present in spring water samples at large concentrations throughout the year. Coliform bacteria in water samples from wells were detected more often and in greater concentrations in July (1995) than in April (1995), October (1995), or February (1996). The increase in bacterial concentrations in July was probably caused by an increase in the ambient temperature of shallow groundwater and soil water, which in turn stimulated biological activity. Data from MRCHD files indicated that the number of wells contaminated with coliform bacteria increased rapidly beginning about 1987 and stabilized in the mid-1990s. We attribute this trend to the increase in residential development in Monroe County, which also began about 1987. Bacterial species present in contaminated wells were consistent with those present in human and livestock wastes. The practice of discharging bacteria-laden septic effluent directly into sinkholes is thought to be a significant source of bacterial contamination to the shallow karst aquifer and, consequently, to private wells and karst springs.

Nitrate concentrations in well water were greatest at the margins of karst terrain and near the ends of streams draining the upland areas of Monroe County. The reasons for this distribution are unclear, but the concentrations appear to be related, in part, to surface-water discharge to the Mississippi River valley. Nitrate concentrations in spring water exceeded natural background concentrations in 92% of the spring water samples and 31% of all the well water samples collected along the

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east-west transects. Water samples from wells and springs rarely, however, contained NO_3^- (as N) at concentrations exceeding U.S. EPA drinking water standards of 10 mg/L.

The frequency of occurrence and the concentrations of pesticides were greater in the well water samples collected in April than in either July or October of 1995. The large number of pesticide detections in April probably resulted from the application of pesticides on croplands during spring planting operations and the subsequent movement of the pesticides into the aquifers by spring rains. Concentrations of pesticides in water samples from springs and wells showed a similar response to the timing of pesticide applications. Relatively small but detectable concentrations of atrazine and alachlor persisted in most springs and a few wells throughout the year. The largest concentrations of alachlor and atrazine in springs were 16 and 98 $\mu\text{g/L}$, respectively; the largest concentrations in wells were 0.56 and 1.6 $\mu\text{g/L}$, respectively. Levels of atrazine and alachlor did not exceed the U.S. EPA MCL of 3 $\mu\text{g/L}$ and 2 $\mu\text{g/L}$, respectively, in any of the well water samples collected during the investigation.

Table 8 Alachlor and atrazine concentrations ($\mu\text{g/L}$) for well transects A, B, and C.

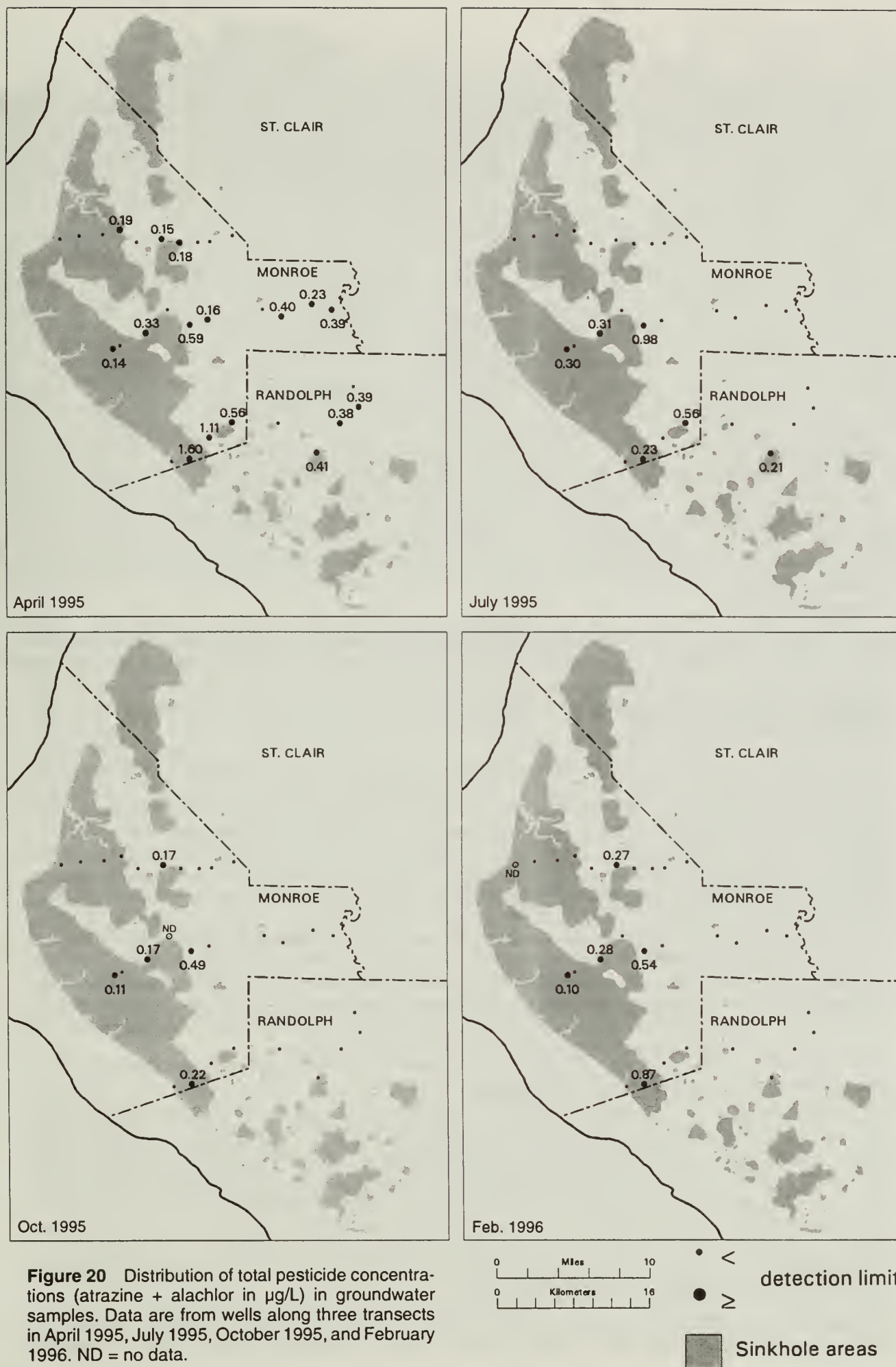
April 1995			July 1995			October 1995			February 1996		
Sample	Alachlor	Atrazine	Sample	Alachlor	Atrazine	Sample	Alachlor	Atrazine	Sample	Alachlor	Atrazine
1A	BDL	BDL	1A2	BDL	BDL	1A3	BDL	BDL	1A4	ND	ND
2A	BDL	BDL	2A2	BDL	BDL	2A3	BDL	BDL	2A4	BDL	BDL
3A	BDL	BDL	3A2	BDL	BDL	3A3	BDL	BDL	3A4	BDL	BDL
4A	BDL	0.19	4A2	BDL	BDL	4A3	BDL	BDL	4A4	BDL	BDL
5A	BDL	BDL	5A2	BDL	BDL	5A3	BDL	BDL	5A4	BDL	BDL
6A	BDL	0.15	6A2	BDL	BDL	6A3	BDL	0.17	6A4	BDL	0.27
7A	BDL	0.18	7A2	BDL	BDL	7A3	BDL	BDL	7A4	BDL	BDL
8A	BDL	BDL	8A2	BDL	BDL	8A3	BDL	BDL	8A4	BDL	BDL
9A	BDL	BDL	9A2	BDL	BDL	9A3	BDL	BDL	9A4	BDL	BDL
10A	BDL	BDL	10A2	BDL	BDL	10A3	ND	ND	10A4	BDL	BDL
1B	BDL	0.14	1B2	0.15	0.15	1B3	0.11	BDL	1B4	0.10	BDL
2B	BDL	BDL	2B2	BDL	BDL	2B3	BDL	BDL	2B4	BDL	BDL
3B	0.17	0.16	3B2	0.19	0.12	3B3	0.17	BDL	3B4	0.13	0.15
4B	BDL	BDL	4B2	BDL	BDL	4B3	ND	ND	4B4	BDL	BDL
5B	0.21	0.38	5B2	0.25	0.73	5B3	0.23	0.26	5B4	0.17	0.37
6B	BDL	0.16	6B2	BDL	BDL	6B3	BDL	BDL	6B4	BDL	BDL
7B	BDL	BDL	7B2	BDL	BDL	7B3	BDL	BDL	7B4	BDL	BDL
8B	BDL	0.40	8B2	BDL	BDL	8B3	BDL	BDL	8B4	BDL	BDL
9B	BDL	0.23	9B2	BDL	BDL	9B3	BDL	BDL	9B4	BDL	BDL
10B	BDL	0.39	10B	BDL	BDL	10B3	BDL	BDL	10B4	BDL	BDL
1C	BDL	BDL	1C2	BDL	BDL	1C3	BDL	BDL	1C4	BDL	BDL
2C	BDL	1.60	2C2	BDL	0.23	2C3	BDL	0.22	2C4	BDL	0.87
3C	BDL	1.11	3C2	BDL	BDL	3C3	BDL	BDL	3C4	BDL	BDL
4C	BDL	0.56	4C2	0.56	BDL	4C3	BDL	BDL	4C4	2.40	BDL
5C	BDL	BDL	5C2	BDL	0.21	5C3	BDL	BDL	5C4	BDL	BDL
7C	BDL	0.41	7C2	BDL	BDL	7C3	BDL	BDL	7C4	BDL	BDL
8C	BDL	0.38	8C2	BDL	BDL	8C3	BDL	BDL	8C4	BDL	BDL
9C	BDL	0.39	9C2	BDL	BDL	9C3	BDL	BDL	9C4	BDL	BDL
10C	BDL	BDL	10C2	BDL	BDL	10C3	BDL	BDL	10C4	BDL	BDL
PD	6.9	55.2		13.8	17.2		11.1	11.1		14.3	14.3
PDT		55.2			20.7			18.5			21.4

BDL = below detection limits (< 0.1 $\mu\text{g/L}$)

ND = not determined

PD = percent detection of each pesticide

PDT = percent detection for total pesticides (alachlor + atrazine)



Well Construction

Well construction techniques may have led to some of the elevated concentrations of bacteria, NO_3^- , and pesticides in groundwater samples collected from wells in the study area. Wells in Monroe and Randolph Counties are typically constructed in accordance with the well construction code for wells drilled in “creviced formations” with “drift or earth cover” thicker than 9.1 m (30 ft) (Illinois Department of Public Health 1994). The thickness of the regolith cover in the study area is typically greater than the required minimum for this type of well. Bedrock may, however, be exposed at the bottom of nearby sinkholes. Typically, a well is constructed by drilling and casing through the regolith, and the casing is seated, with a drive shoe, into the underlying carbonate bedrock (fig. 21). The annulus around the well casing is filled with a clay slurry, bentonite, or cement grout, and drilling continues deeper into bedrock. If large voids are encountered, they may be cased. However, the borehole is typically left open to take advantage of multiple fissures, fractures, and solution channels that produce water. Available well construction data for the 33 wells sampled during this investigation indicate that the depth to which most wells were cased below the carbonate bedrock–regolith interface was between 1 and 4 m (3.3 and 13 ft) (appendix: table A1).

Even if wells are cased to depths that preclude the possibility of infiltration by near-surface contaminants, corrosion of steel well casing or failure of the grouting along the annulus between the casing and bedrock can result in leaks, thus allowing contaminants to enter the well system. As shown in figure 21, construction practices and/or material failures can allow water to enter a well along preferential flow paths such as those found near the base of the regolith, or in any part of the well bore. A downward hydraulic gradient could induce groundwater from sources near the top of the borehole to flow down the borehole and enter hydraulically conductive features lower in the borehole. Thus, the natural chemical profile of the aquifer would be disrupted. The bedrock near land surface in the study area is dominated by karst features that receive water from surface runoff through sinkholes, water from smaller macropores in the regolith, and water that slowly percolates through the regolith.

The observed seasonal variations in the occurrence and concentration of bacteria and pesticides in water samples collected from transect wells support our contention that well construction practices have led to the inflow of shallow contaminated groundwater from karst areas into the wells. Seasonal changes in these contaminants would not be so evident if the wells were receiving only groundwater from deeper in the aquifer.

Observations in nearby quarries and outcrops indicated that solution-enlarged openings in the limestone bedrock are generally larger and better developed in the shallow bedrock about 10 to 15 m (33 to 50 ft) below the regolith–bedrock interface than in the deeper bedrock. Groundwater can potentially enter a well more readily from solution-enlarged fissures and conduits along bedding planes near the bedrock surface than from the more subtle fissures deeper in bedrock. In most cases, the shallower zones in the karst aquifer should have a greater potential to contain groundwater with larger concentrations of bacteria, NO_3^- , and pesticides than would the deeper zones.

Casing and grouting of wells through the shallow karst aquifer to depths of 10 to 15 m (33 to 50 ft) below the bedrock–regolith interface may help to reduce the occurrence of at least some of the groundwater contamination of wells in the study area. Unfortunately, the shallow karst aquifer may be the dominant source of groundwater in some areas. Therefore, casing off the upper part of the aquifer could result in deeper, but much less productive wells, in which the water quality may be improved, but the yield of the well may be too low for household use.

Recommended Sampling Techniques

The responsibilities of the MRCHD include monitoring water quality in Monroe and Randolph Counties for contaminants that include coliform bacteria and NO_3^- . The agency has recently also shown interest in the occurrence of pesticides in well water, as well as bacteria and agricultural chemicals in spring water. Because of their responsibilities and interest, and because of the findings of this investigation on the occurrence of these contaminants in southwestern Illinois, we recommend the following guidelines to enhance the efficacy of the MRCHD’s water-sampling program.

The suggested sampling program may be divided into two tasks: (1) routine water well sampling and (2) long-term water well and spring sampling.

(1) Routine water well sampling for coliforms and NO_3^- should be conducted with consideration for the seasonal variability of the occurrence of coliforms in groundwater in Monroe and Randolph

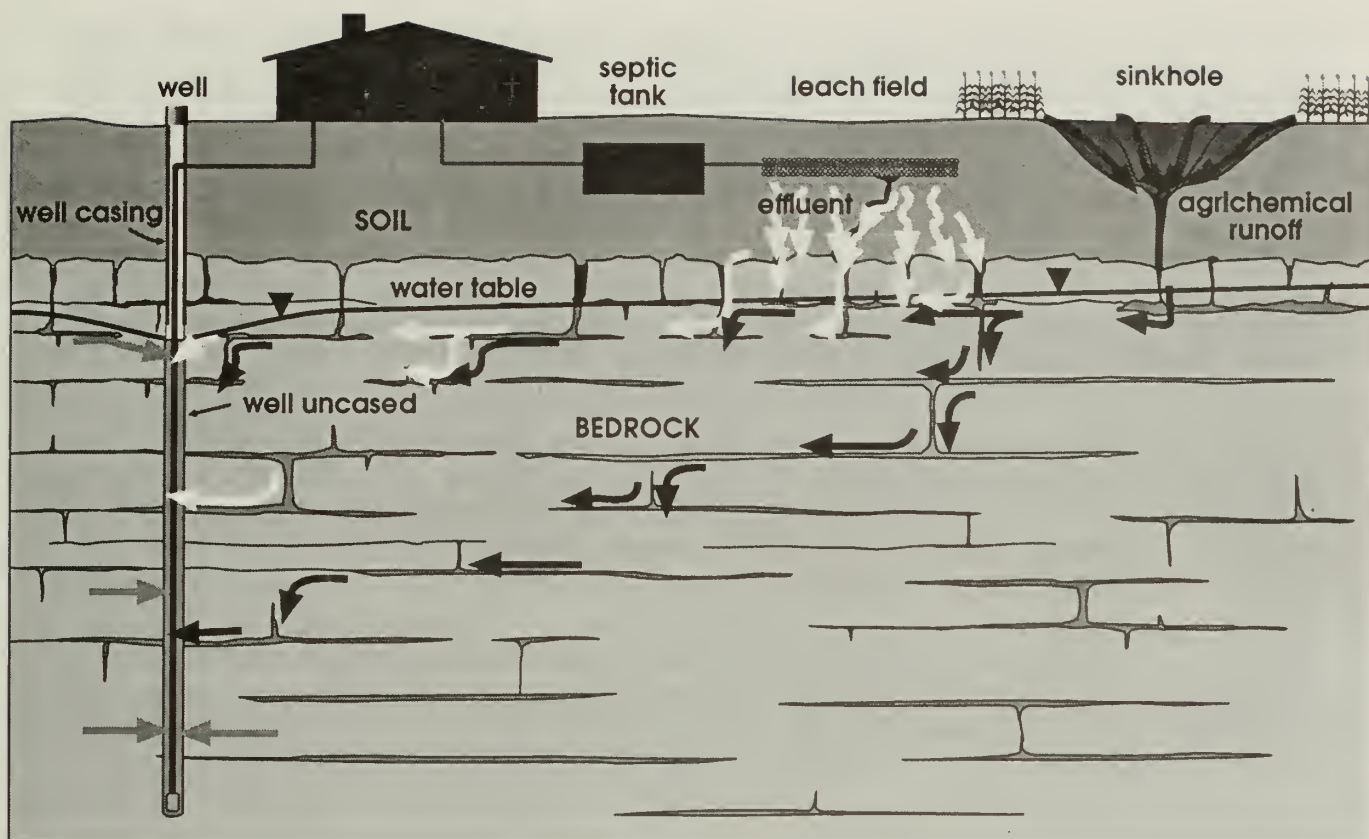


Figure 21 Conceptual model of potential routes of contaminant migration from a leach field and sinkhole to a well, cased through the soil zone and a few meters of bedrock, and uncased deeper in bedrock. The water table has been simplified. White arrows indicate septic effluent, black arrows indicate agricultural chemicals, and gray arrows indicate clean water.

Counties. We recommend that routine sampling of private wells be conducted during midsummer when warm temperatures accelerate bacterial growth in surface water, soil water, and shallow groundwater. Analysis of water samples for NO_3^- can also be conducted at this time because its concentrations in wells do not appear to be seasonally dependent.

(2) Long-term well-water and spring sampling for coliform bacteria, NO_3^- , and pesticides in Monroe and Randolph Counties would yield information on annual changes in the level of contaminants entering local groundwater. We recommend that sampling of a select group of private wells and springs be conducted on a regular basis to identify long-term trends in groundwater quality and monitor temporal changes. Because of the techniques used to construct private wells in creviced rock, these wells could serve as indicators of water quality for the shallow aquifers. Drillers' logs having detailed descriptions of the soils, rock types, and construction techniques used for each well sampled should be examined. The casing depth and water analyses could be used to estimate the depth of infiltration of contaminants into bedrock aquifers, especially in areas where wells are cased through the regolith and the upper parts of the shallow karst aquifer. Springs in the two counties could be used as indicators of the degree of contamination in the shallow aquifers.

Selected wells should be sampled twice a year to ensure that representative water samples for each potential contaminant are collected. As with the routine well-water samples, water samples should be collected and tested for bacterial contamination during midsummer. Well-water sampled for pesticides should be collected within several weeks following pesticide application to croplands, optimally after the first rainfall when increased flow from runoff is observed in nearby springs. Wells in the same basin as tested springs could also be sampled, thereby allowing the water quality of the shallow karst aquifer to be compared with that of the selected wells.

The collection of representative water samples from springs is difficult because of uncertainty about the extent and location of the groundwater basin feeding a particular spring, the difference in recharge areas during flood events, and the types of water samples collected (Quinlan 1990). Rather than performing a survey-type study in which a large number of water samples are collected from springs for which there is little information available on sources of the water, we recommend that long-term groundwater monitoring efforts focus on springs that discharge from known flow systems.

By knowing the approximate location of a groundwater basin, it should be possible to identify land use in the basin area and relate the land use to observed water quality. Frequent sample collection, approximately one grab sample every 2 weeks, should be adequate for the purposes of the MRCHD. Grab samples, although not an ideal sampling method, showed trends similar to samples collected using the long-term sampling techniques employed in this investigation. Grab samples have been used effectively by Rowden et al. (1993) in a multi-year study of Big Spring in the karst region of northeastern Iowa. Measurements of spring discharge, temperature, and specific conductance at the time of sampling would help interpret the water quality data. As more of the groundwater basins are delineated in Monroe and Randolph Counties, additional springs can be selected and sampled. Such an approach would yield a quantitative estimate of the mass of nitrogen and pesticides entering the groundwater flow system and ultimately discharging into surface water systems.

APPENDIX SITES SELECTED FOR GROUNDWATER SAMPLING

Springs and wells for collecting groundwater samples were chosen on the basis of their location with respect to karst features in Monroe County (fig. A1). Sites were selected in areas of mature karst terrains and in areas containing no karst features. A brief description of each site and information on the geology and hydrogeology of the sites are presented below. Adjacent to each site name is the identifying letter or letters that appear in fig. A1.

Springs

Nine springs and a cave stream were selected as sampling sites on the premise that water samples collected from springs generally are more representative of karst aquifers than those taken from wells. Most water in a karst aquifer moves through relatively large fissures and conduits ranging from about 1 cm (0.4 in.) wide to more than 5 m (16.4 ft) in diameter. Fissures and conduits such as these drain a high percentage of the aquifer (Quinlan 1988). The chemical composition of water samples from the springs represented groundwater circulating within the shallow karst aquifer. Because of the manner in which wells are constructed in the study area, the composition of water samples from wells was compared with those from springs as an indicator of the possible source of groundwater to the wells.

Many of the springs we sampled are described as (1) cave springs because they are the discharge point for extensive cave systems or (2) karst windows because they are fragments of cave streams exposed by collapse of the cave roofs. There is little genetic difference between, for example, the Illinois Caverns cave stream and May's Spring karst window. Geologic formations that host the springs and cave stream were determined using geologic maps prepared by Weller and Weller (1939). The springs are listed from north to south.

Andy's Run Spring (A)

Location: Sec. 16, T2S, R10W

This cave spring flows from the base of an outcrop within a dissected ravine in upper St. Louis or basal Ste. Genevieve Limestone. The spring issues from the cave and disappears into the stream bed about 50 m (164 ft) from the mouth of the cave. The cave was mapped by Moss et al. (unpublished cave map, 1995) and extends in a south-southwest direction into the highlands for about 120 m (394 ft). The terrain overlying the cave is a mixture of covered karst and karst terrain that was being transformed from croplands to residential use at the time of this investigation. A seepage sampler was installed at this site, and long-term and grab samples were collected on a monthly basis in 1995.

Unnamed Spring (U)

Location: Sec. 21, T2S, R10W

This spring is located at the base of a hill on the floodplain of Fountain Creek in the upper St. Louis Limestone. The spring was reported by the owner to produce approximately 47 L/s (740 gpm) at base flow. An elliptical pond was created to capture water from the spring for irrigation purposes. The owner has installed an electrical substation and pump at the site, and the overflow of the pond discharges into a stream that empties into nearby Fountain Creek. The pond was reported to be 3 m (9.8 ft) deep near the spring outlet, which is a cave entrance that was approximately 0.3 m (1 ft) high and 2 m (6.6 ft) wide prior to construction of the pond. Water samples were collected from the spring in 1994 as grab samples and by using an ISCOTM sampler and a seepage sampler.

Boy Scout Camp Spring (BS)

Location: Sec. 21, T2S, R10W

This spring discharges from a small cave at the base of a 12- to 14-m-high (40–45 ft) bluff in the upper St. Louis Limestone. The spring flows directly into Fountain Creek through an entrenched channel. Another cave spring is located just to the west of this spring along the same bluff. Discharge from both springs may be characterized as a high-energy turbulent flow following large rainfalls. Discharge from the latter spring is almost negligible during the dry summer months.

During base flow, the specific conductances and temperatures of the water measured at these adjacent springs were distinctly different. At high flow (during and following a rainfall that initiated runoff), however, the chemical parameters of the water from both springs were identical, indicating that conduits leading to the springs allowed mixing at levels higher in the aquifer than those that supply the spring at base flow. Grab samples were collected monthly from Boy Scout Camp Spring.

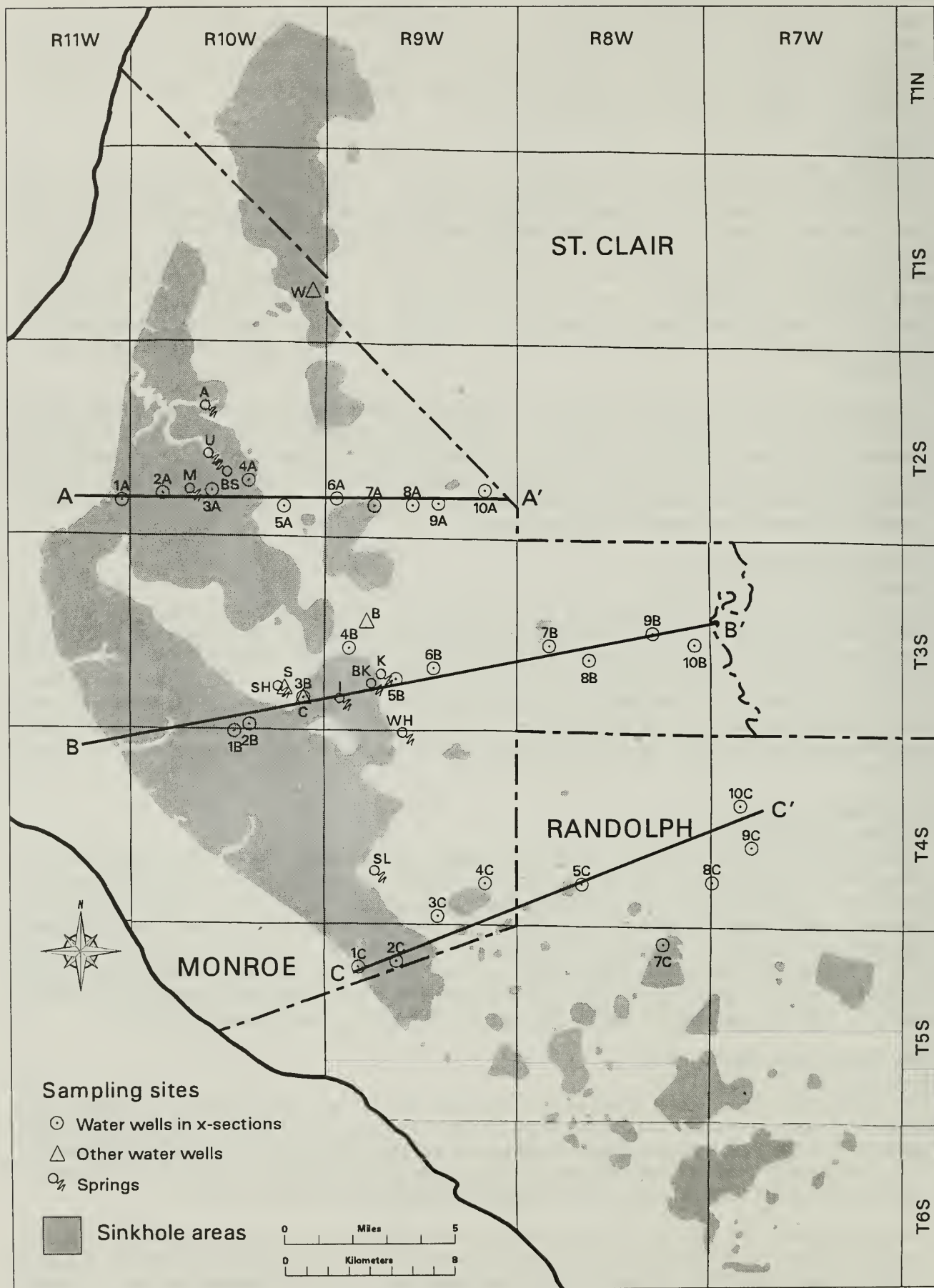


Figure A1 Map of the study area showing karst regions (sinkhole areas), sampling locations, and lines of cross sections. Identifiers for wells are in table A1 and in the text.

Only one sample was collected from the adjacent spring in 1994. Measurements of field parameters of spring water were taken from both springs on a routine basis.

May Spring (M)

Location: Sec. 29, T2S, R10W

This spring is a karst window (or fenster) formed by the collapse of a cave roof in the middle St. Louis Limestone. The spring consists of an elliptical pool about 2 m (6.6 ft) deep at base flow. The water flows from a submerged cave to the west into the spring and then disappears into a small, exposed cave to the east. The surrounding area is karst farmland. The spring exhibited pipefull flow during and following heavy rains, with waters rising to as much as 8 m (26 ft) above base-flow water level and water flowing in two directions along a normally dry stream bed. The owner stated that the spring would periodically discharge relatively large volumes of air during periods of high flow. This high-energy system entrained cobbles 12 to 14 cm (4.7–5.5 in.) in diameter and deposited them on one bank of the spring several meters above base flow. A small swallow hole leading to the cave system, located just west of the spring, received runoff from adjacent croplands and woods. A seepage sampler was installed at this site, and long-term and grab samples were collected on a monthly basis in 1995.

Solich Spring (S)

Location: Sec. 26, T3S, R10W

Solich Spring (fig. A2) is located in an area that exhibits no karst features even though the underlying bedrock strata are the middle St. Louis Limestone. The overlying soil includes about 7 m (23 ft) of loess and clay-rich regolith. The site is located 10 km (6.2 mi) south of Waterloo in the low-lying valley of Dry Run Creek. Water from the spring rises to a land surface that is approximately 1 m (3.3 ft) above an adjacent dry creek bed. This spring and others like it constitute the major sources of

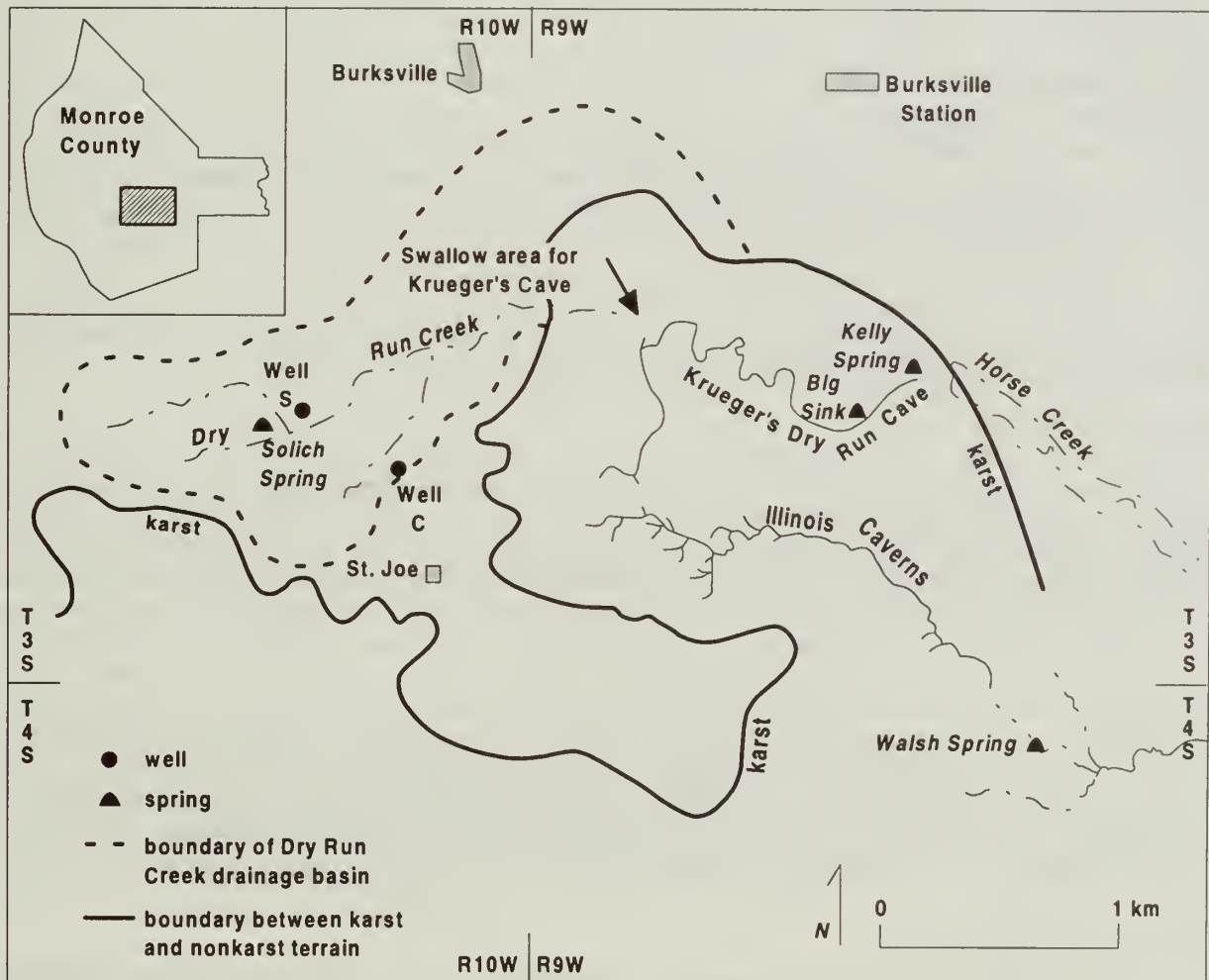


Figure A2 Map of the drainage basin of Dry Run Creek and its geographic relationship to Krueger's Dry Run Cave. The locations of four springs, the cave stream, and two wells used as sampling sites are included in this map. Cave map is modified from Frasz (1983).

water for Dry Run Creek during base-flow conditions. The creek flows to a swallow hole that, according to cave maps (Frasz 1983), intersects the beginning of Krueger's Dry Run Cave. A newspaper article by Wightman (1967), described early exploration of this cave and how it was physically and hydraulically connected to Dry Run Creek. On the basis of its chemical composition and relatively high head, we suspect that groundwater discharging from Solich Spring originates, to a large extent, from bedrock. A seepage sampler was installed in this spring, and grab samples were collected monthly in 1994.

Big Sink Spring (BK)

Location: Sec. 29, T3S, R9W

This is a large, steep-sided sinkhole that formed in 1 to 2 m (3.3–6.6 ft) of regolith overlying upper St. Louis Limestone. The sinkhole is actually a karst window that formed as a result of a roof collapse of Krueger's Dry Run Cave (fig. A2). The chemical composition of water samples from this site was identical to those of Kelly Spring located approximately 0.7 km (0.43 mi) to the northeast, and the spring was found to be hydraulically connected with Kelly Spring (Frasz 1983). A seepage sampler was installed at this site, and long-term and grab samples were collected on a monthly basis in 1995. Because water samples from both Kelly Spring and Big Sink had chemical compositions that were identical regardless of stage, the data were grouped in a single data set.

Kelly Spring (K)

Location: Secs. 28 and 29, T3S, R9W

Kelly Spring is located on the property of the Waterloo Sportsmans Club at the base of a steep hill and exposure made up of upper St. Louis Limestone. The spring discharges from Krueger's Dry Run Cave and is the headwaters of a tributary of Horse Creek (fig. A2). Water discharges from the cave and flows under a natural bridge that was used as a point for measuring water levels. High-energy turbulent conditions were characteristic of this spring following large rainfalls. Seepage samplers were installed at this site during and following rain events, and numerous grab samples were collected in 1994.

Illinois Caverns (I)

Location: Sec. 31, T3S, R9W

Illinois Caverns (fig. A2) is a State Natural Area initially mapped by Bretz and Harris (1961). It is a relatively large trunk cave formed by the dissolution and enlargement by groundwater of a channel along a bedding plane in the St. Louis Limestone (Panno et al., in press). The cave consists of more than 8 km of traversable passage (Frasz 1983), and a stream flows down the center of the cave. The terrain above Illinois Caverns is predominantly karst and is dominated by croplands. A dye-tracing experiment indicated that at least some of the water discharging from the cave exited at a spring located about 0.8 km (0.5 mi.) east of Walsh Spring (P. Wightman, unpublished report, 1969). Grab samples were collected from this site near the main entrance.

Walsh Spring (WH)

Location: Sec. 4, T4S, R9W

Walsh Spring is located at the base of a crescent-shaped bluff that it shares with Walsh Cave. The spring and cave discharge from limestone of the Aux Vases Formation. Walsh Spring discharges from a dry stream bed that appeared on cave maps to be at the end of Illinois Caverns (fig. A2). Although Walsh Spring was reported to be the discharge point for Illinois Caverns (Frasz 1983), we could find no references of previously conducted tracer tests that would have supported this hydraulic connection. The chemical composition of time-synchronous water samples collected from Illinois Caverns and Walsh Spring suggested that they either were not in hydraulic communication or that waters from Walsh Spring represented a mixture of water from Illinois Caverns and other sources. The water in nearby Walsh Cave typically had a much lower discharge rate, a significantly larger specific conductance and alkalinity (as CaCO_3), and a lower temperature than either Illinois Caverns or Walsh Spring. These data suggest that Illinois Cavern has no hydraulic connection to either Walsh Spring or Walsh Cave under base-flow conditions. A seepage sampler was installed at Walsh Spring, and long-term and grab samples were collected on a monthly basis.

Sensel Spring (SL)

Location: Sec. 29, T4S, R9W

This spring flows up from a small opening in an exposure of upper Renault Limestone near a dry creek bed and into a concrete well house. The spring is the headwaters of a small stream in the barnyard of a farmstead. Water emanating from the spring is used for household and farm supplies. The piezometric surface of the spring water was at least 2 m (6.6 ft) above the land surface; overflow

discharged through a pipe in the side of the well house. The owner, who routinely kept a record of daily rainfall, stated that discharge may increase slightly following heavy rainfalls. The nearest karst features in relation to the spring are 0.8 km (0.5 mi) to the southwest. An ISCOTM sampler and seepage sampler were installed at this spring; long-term and monthly grab samples were collected in 1994 and 1995.

Just before we began sampling in 1994, the well house foundation began to leak as a result of the activities of crayfish. At that point, the water level in the well house dropped from a depth of about 2 m (6.6 ft), where it overflowed through a conduit in the side of the well house, to a depth of 1 m (3.3 ft), where it seeped out from under the foundation of the well house. Coliform bacteria were present in the spring water until the foundation was repaired. Following the repairs, subsidiary springs developed in the barnyard, and the bacterial content of the spring water in the well house was negligible. Apparently, lowering of the piezometric surface of the underlying aquifer had allowed animal wastes to enter the aquifer up gradient of the spring.

Selected Wells

Four wells were selected for monthly sampling in 1994 on the basis of their locations relative to karst features (fig. A1) and croplands and because water samples from three of the wells consistently contained NO₃⁻ concentrations that exceeded the U.S. EPA MCL of 10 mg/L (as N) for drinking water. We hoped that sampling these wells would yield some insight into the source(s) of NO₃⁻ contamination in the study area.

Well W (W)

Location: Sec. 25, T1S, R1W

Well W is located in a karst area surrounded by cropland. The well is 62 m (203 ft) deep, and its water became cloudy to muddy during and following heavy rainfall (2.5 cm (1.0 in.)/day) or when lawns were watered and/or cars were washed. Other residents in the vicinity reported similar problems. The well was reported to pump a total of 0.95 L/s (15 gpm) (0.25 L/s [4 gpm] from one fissure and 0.70 L/s [11 gpm] from another; unpublished driller's log). Water samples from the well contained coliform bacteria, and the water is used only for washing. The throat of a relatively large sinkhole near the well collected drainage from the yards of several adjacent houses and effluent from two aeration-type septic systems. Such an arrangement is common in Monroe County. Runoff and waste water were often ponded in the sinkhole and typically produced an odor of septic effluent. Water samples from this well were collected monthly and during and following a particularly intense rainfall in 1994.

Well S (S)

Location: Sec. 26, T3S, R10W

Well S is the deeper of two wells located within an area covered with loess and clay-rich materials. No karst features were observed within 1 km (0.62 mi) of the wells (fig. A2). Well S is 36 m (118 ft) deep and open to limestone bedrock. The owner stated that he had problems with iron buildup on the well screen and periodically used bleach to keep the screen from clogging. This well was sampled monthly and during and following an intense rainfall in 1994.

The shallower, bored well is 10 m (33 ft) deep and screened in unconsolidated materials. The well was located adjacent to a hog-containment facility and was sampled only once in 1994. The well was found to contain fecal coliform bacteria, a Cl⁻ concentration of 151 mg/L, and a NO₃⁻ concentration of 15.3 mg/L.

Well C (C)

Location: Sec. 26, T3S, R10W

Well C is located in an area with about 15 m (49 ft) of loess and clay-rich regolith that contained no karst features (fig. A2). The well is located, however, within 0.25 km (0.15 mi) of karst terrain and is surrounded by cropland. The 17-m-deep (56 ft) well bottoms in fractured limestone bedrock. Water from this well was known to contain unacceptably large NO₃⁻ concentrations. This well was sampled monthly and during and following an intense rainfall in 1994. It was also sampled as one of the wells (3B) along the three transects in 1995.

Well B (B)

Location: Sec. 17, T3S, R9W

Well B is located in a nonkarst area bounded on the north, south, and west by karst terrain slightly less than 1 km (0.62 mi) away. The well is 36 m (118 ft) deep and drilled in limestone. The owner

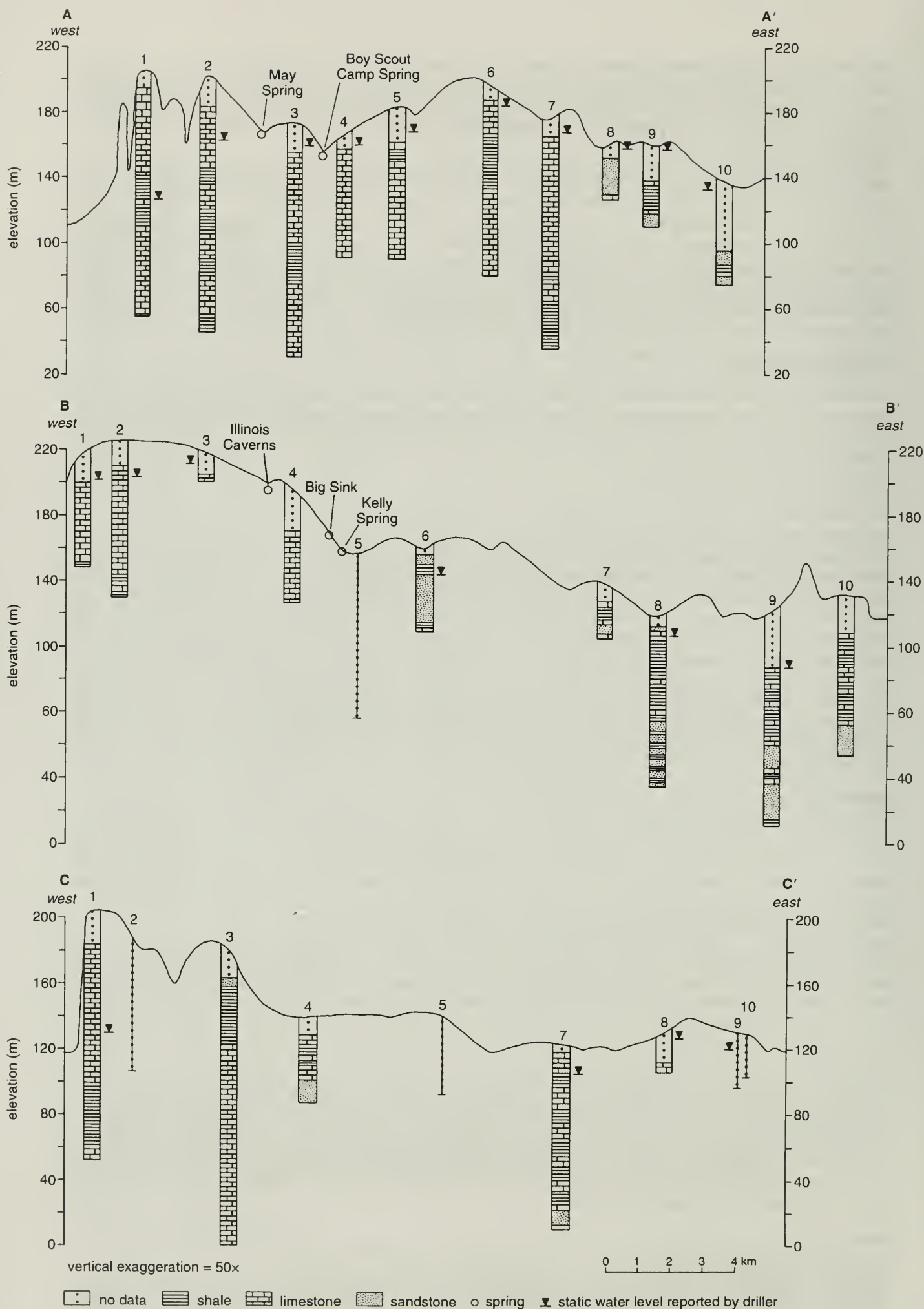


Figure A3 Cross sections from transects A, B, and C showing lithologies of most wells and locations of springs sampled during this investigation. Locations of cross sections are shown on figure A1.

reported having difficulties with the well since it was drilled because of the presence of coliform bacteria and NO_3^- . The owner also stated that the land in the vicinity of the well had been used in the past for cattle confinement. The land just east of the well was used as cropland at the time of this investigation. This well was sampled monthly and during and following an intense rainfall in 1994.

Well Transects

Twenty-nine wells located along three east–west-trending transects were selected and sampled in April, July, and October of 1995 and February of 1996. The wells were as evenly spaced as possible along each transect and were in close proximity to several springs sampled during the investigation. The well locations extended from the bluffs of the Mississippi River in the predominantly karst western part of Monroe County to the nonkarst eastern parts of Monroe and Randolph Counties (fig. A3). Transects were assigned the letters of A, B, and C from north to south. Wells in individual transects typically were between 1 and 3 km (0.62 and 1.9 mi) apart, but some were as much as 6 km (3.7 mi) apart. The transect lines were between 10 and 12 km (6.2 and 7.4 mi) apart. Available construction data for each well were compiled and summarized (table A1). Cross sections showing lithologies of each well along each transect and static water levels (reported by the drillers) were constructed. They reveal the lithologies intersected by each well (fig. A3). Because of well construction methods, most water levels were composites of the entire borehole starting just below the bedrock surface. Consequently, the water levels reflected the transmissivity of the aquifers intersected and revealed only general trends in groundwater flow to the west in karst terrain near the Mississippi River valley and to the east and southeast in the east half of the county.

The well sites represent the various geomorphological settings in Monroe and Randolph Counties. The distribution of these sites throughout the study area is presented in fig. A1. Well C from the selected well series was designated Well 3B because it was intersected by the B transect at the desired point and no other wells were available, due to the paucity of residents in the area.

Table A1 Details of well construction for transect wells 1A to 10C and four selected wells.

Well no.	Depth (m)	Elevation (m)	Casing type	Cased depth (m)	Static WL (m)	Date drilled	Aquifer lith.	Soil thick. (m)	Karst terrain	Driller	Driller's comments on well log
1A	151	204	6" steel	26	77	1974	Ls	12	Y	Haudrick	Water from limestone.
2A	154	198	6" PVC	18	40	1990	Ls	17	Y	Miller	Water from limestone at 99–101 m.
3A	142	160	PVC, steel	20	18	1987	Ls	12	Y	Chitwood	Water from limestone at 20–73 m. 1.5 m rubble zone at 18 m.
4A	44	168	6" steel	14		1990	Ls	12	Y	St. Charles	Water from 40–41 m. Grouted with cuttings and bentonite 0–40 m.
5A	93	183	6" PVC	24	15	1994	Ls	21	N	St. Charles	Water from limestone at 62–87 m. Well cased to top of shale.
6A		198							M		NR
7A	139	183	6" steel	14	8	1993	Ls	10	Y	Haudrick	None.
8A	35	168	6" steel	13	5	1989	Ss	11	N	Haudrick	Water from sandstone at 13–35 m.
9A	50	165	6" PVC	40	3	1994	Ss	23	N	St. Charles	Water from sandstone 43–50 m. Grouted with cuttings and bentonite.
10A	61	146	6" PVC	18	8	1987	Ss		N	Miller	Water from 44–61 m. Grouted with cuttings only.
1B	70	216	6" steel	21	19	1994	Ls	19	Y	Haudrick	Water from limestone at 55–60 m.
2B	95	226	6" steel	20	21	1988	Ls	14	Y	Haudrick	Annular space grouted with CTGS-Bentonite from 0–12 m.
3B	18	213	6" PVC	14	3	1993	Ls	16	M	Kohnen	Water from cracked limestone at 16–17 m.
4B	68	198	6" PVC	29		1994	Ls	25	Y	Kohnen	Water from cracked limestone at 38 m. Grouted with bentonite.
5B	105	162							M		Information from well owner only.
6B	46	168	6" steel	25	15	1983	Ss	3	N	Haudrick	Water from sandstone at 25–45 m.
7B	73	137	6" PVC	65		1984	Ls	9	M	Kohnen	Grouted with bentonite at 0–65 m.
8B	106	133	5" steel	101	16	1972	Ss	6	N	Haudrick	None.
9B		137							N		NR
10B	98	130							N		Information from well owner.
1C	151	195	6" steel	32	76	1975	Ls	21	Y	Haudrick	Water from 97–104 m. Well at top of bluff.
2C	85	184							Y		Information from well owner only.
3C	178	183	6" steel	59		1978	Ls	18	Y	St. Charles	NR
4C	61	140							M		Information from well owner only.
5C	47	128							Y		Information from well owner only.
7C		140							Y		NR
8C	43	130	6" PVC	9	2	1993	Ls	21	N	Kohnen	Casing slotted from 9–43 m. Water from sandy clay and limestone.
9C	34	131	7" steel	32	9	1993	Ss	11	N	St. Charles	Well screened from 32–34 m in broken rock below sandstone.
10C	26	131					Ls	23	N		Information from well owner only.
Selected wells											
W	62	200	6" PVC	14	12	1978	Ls	11	Y	St. Charles	Water from two fracture zones. Broken rock at 14–30 m.
C	18	213	6" PVC	14	3	1993	Ls	16	M	Kohnen	Water from fissure in gray limestone.
B	38	195				1975	Ls		N	Haudrick	Old well cleaned out. No record of casing.
S	37	213	6" steel	21	2	1979	Ls	22	N	Haudrick	Soil described as 22 m yellow clay.

Aquifer lithology: Ls = limestone, Ss = sandstone

Karst terrain: Y = yes, N = no, M = within 1 km of karst margin

NR = no well record available

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